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THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE WASTE AND CONSERVATION OF PLANT FOOD.¹

BY HARVEY W. WILEY.

ONE of the greatest of the practical problems presented for solution by agricultural chemistry is the conservation of plant food. With an abundance of plant food and a favoring climate, it is difficult to place a limit to the power of the earth for supporting life. We have read much in political economy of the limit of subsistence, and one bold philosopher has based a theory of the limitation of the number of human beings upon the earth on the insufficiency of the earth to support a greater number. Happily, however, the Malthusian philosophy was promulgated before the days of that great agricultural renaissance which has been brought about chiefly through the efforts of experimental agricultural chemistry. I am not so blinded by the achievements of agricultural chemistry as to deny to many other branches of science an important and, in many cases, necessary influence in this development of agricultural science; but I think every candid man will admit that in this development chemistry has always taken the front rank and led the way. This is pre-eminently true of the investigations into the nature and extent of the plant food available on the surface of the earth. In this country, owing to the great stores of wealth which the past had accumulated in the soil, it is only within recent years that the question of the supply of plant food has assumed any practical importance. As long as there

¹ Retiring address of the President of the American Chemical Society, Baltimore Meeting, December 27, 1893.

were virgin fields at the disposal of the agricultural rapist, the conservation and restoration of exhausted fields was of little consequence. The result has been that the wealth of hundreds or, perhaps, thousands of years slowly stored in the soil has been poured forth in a century, not only for the enrichment of this country, but for the benefit of all countries. Unfortunately, or fortunately, these stores are now practically explored and there is little left in this land of virgin fertility to tempt the farmer to new conquests. Not only have these stores of plant food been utilized, but, much to the discredit of the American farmer, they have been wasted. The mark of good agriculture is to see fields yielding annually good returns and increasing, or at least not lessening in fertility. This being true, the history of American agriculture to within a few years must be the history of bad farming, for everywhere we have seen fertile fields losing their fertility and farms once productive abandoned. No difference how great the store may be, if it be continually drawn upon and never replenished, the day will some time come when it will be exhausted. This day has come to a large portion of the agricultural lands of this country and to-day there is an awakening everywhere in regard to the best methods of checking the waste and of restoring what has been lost.

I desire for a brief period, on this occasion, to call the attention of the chemists of this country to some of the methods by which plant food is removed from the fields and some of the direct and indirect ways in which it is and may be returned. On a former occasion¹ I have discussed the extent to which plant food is removed from the soil directly in the crops and the dangers which arise to an agricultural community which continually exports its agricultural products. On that occasion I pointed out the amount of potash, phosphoric acid, and nitrogen per acre annually removed by the crops of the United States, and showed that the only safe agricultural products to send out of a country were sugar, oil, and cotton. It is true that with native, unexhausted soils a country may acquire great wealth by agricultural exports, but the history of the world shows that a

¹ Vice Presidential Address before the American Association for the Advancement of Science, Buffalo, 1886.

country which depends for its wealth and its commerce on agricultural exportation is in the end reduced to pauperism. A single example may serve to accentuate this remark; I refer to the island of Cypress, which two thousand years ago was the granary of many cities bordering on the Mediterranean Sea. Supplying hundreds of thousands of people with corn, it gradually became impoverished, and to-day its soils are perhaps the poorest of any known.

The waste to which I desire to call your attention to-day is not that which normally takes place in the production of a crop, but that which is incidental to the cultivation of the soil and to a certain extent unavoidable. My purpose is to develop, if it be possible, the relations of agricultural chemistry to this waste, with the purpose of pointing out a course by which it can be returned and in what way we may at least reduce to a minimum the unavoidable removal of valuable plant food. You have all, perhaps, surmised the character of this waste; I refer to the denudation of fields by water and to the removal of soluble plant food by the percolation of water through the soil.

The losses due to the denudation of fields are purely of a mechanical character. The natural forest, or the natural covering of grass over an area of soil, prevents, to a large extent, the denudation due to heavy downpours of rain. The removal of the forest, and the destruction of the grass by cultivation, leave the soil in a condition in which it is unable to resist the action of flowing surface water. The muddy character of the water in all streams bordering on cultivated hilly fields after a heavy rain storm is a familiar instance of the tremendous energies which are exerted by a heavy downpour of rain in the carrying of the soil into the streams and its transportation towards the sea.

It is not necessary to emphasize the fact that the agricultural chemist is practically powerless to prevent the surface erosion due to heavy rains, but a few practical lessons derived from the application of chemical discoveries to the soils show how, in a certain measure, even surface erosion may be controlled, or at least reduced to a minimum by the application of the principles

of culture founded upon the facts disclosed by advanced science.

The observing agriculturist will have noticed that even in a hilly country a soil *in situ* underlaid by limestone is less likely to be cut up by gullies than a soil similarly situated and deficient in carbonate of lime. The reason of this is plain. In a soil deficient in lime the clays when once brought into suspension by moving water assume a semi-colloid state and remain indefinitely in suspension. Clays, on the other hand, which are heavily impregnated with lime salts are in a flocculated state, and the larger aggregates thus produced settle quickly. The result of this is that such a soil is less easily moved by water, and a field thus treated less exposed to washing by heavy rains.

Our knowledge of flocculation and its physical and chemical results is due largely to the investigations of Shulze, Schloesing, and Hilgard, and the results of their researches have shown in a most emphatic way the beneficial changes which take place, especially in stiff clay soils, by the application of lime.

It is thus an incontrovertible fact that the surface washing of cultivated fields, especially if they be naturally deficient in lime, could be greatly diminished and has been greatly diminished by the free application of this substance.

The change in the physical condition of the soil, which is produced by the lime, is also another important factor worthy of consideration. A stiff clay soil is almost impervious to the penetration of surface water and thus the amount which is carried off is raised to a maximum. A well limed soil, on the contrary, in which the particles are perfectly flocculated, is much more pervious and the amount of water which will be retained and delivered gradually to vegetable growth is much greater. Thus the beneficial effects of lime are manifested in both ways; in the better retention of the flocculated clays and in increasing the capacity of the soil for holding a given amount of water in its interstitial spaces.

There are many other salts which also have the same properties as those of lime, but I have spoken of lime salts chiefly because they are cheaper and, therefore, more economically applied. Perhaps next to lime, common salt would be the most

efficient in producing the results already described; but common salt being extremely soluble would soon be leached out of a soil. On the other hand, lime, even when supplied as hydrate, in which case it is somewhat soluble, quickly becomes converted into a carbonate which is practically insoluble in water which does not contain an excess of carbon dioxide.

I am aware of the fact that liming to prevent erosion by surface drainage has not been emphasized as an example of the benefit of the proper chemical treatment of soils, yet I feel sure that all who will give the subject a thoughtful consideration will agree with me in saying that this aspect of the subject is one of no small importance, especially when considered in respect of hilly fields, and even of fields of more level surface.

Without dwelling long upon this point, it is only necessary to call your attention to the immense quantities of soil material annually conveyed to the sea by the causes of erosion already mentioned to show what an active and powerful foe the farmer has in this source of loss. Anyone who watches, even for a short time, the volume of water carried by the Mississippi into the Gulf of Mexico will have a most effective object lesson in regard to this source of loss.

A more striking lesson may be seen in the hill regions bordering both banks of the Ohio river. Hundreds of fields once covered with sturdy forests of oak, maple, and walnut, and afterwards bearing large crops of maize, tobacco, and wheat, may now be seen furrowed with gullies, as with the wrinkles of age, and abandoned to brush and briers. The same is doubtless true of other hill regions, but I speak the more advisedly of those which have come under my personal observation.

Great, however, as the mechanical loss of plant food is, it is by no means as dangerous as the loss of the soluble materials caused by the percolation of the water through the soil. The study of the nature of the loss of these soluble materials, together with the estimation of their amount, forms the subject of lysimetry. Agricultural chemists have used many devices for the purpose of determining the character and amount of the natural drainage of soils. Evidently the treatment of a specially prepared portion of soil by any solvent, although giving in-

teresting results, does not indicate the natural course of solution. The only way in which this can be determined is to be able to collect, measure and study the character of the drainage from a given portion of the arable surface of the earth *in situ* and under normal conditions. Various methods of lysimetric investigation have been proposed and used, all of them possessing many points of value.

An excellent system of such observation has been established, for instance, at the Agricultural Experiment Station of Indiana. It is not my purpose, however, to discuss the mechanical details of lysimetry, but only to call your attention to the main principles which underlie it. The movement of water near the earth's surface is a matter of especial interest to agriculturists. Whitney¹ has clearly pointed out that the little excess or deficiency of water is of far more importance to the growing crop than the quantity of the excess or deficiency of its other foods. Soils richest in plant food will produce a small harvest if there be a great excess or deficiency of water, while soils which are poor in plant food will produce an abundant crop if the water be present in proper amounts and have proper and timely access to the rootlets of the plant. The study, therefore, of the water movement in the soil, whether laterally, upward, or downward, is of the utmost practical importance. The methods of a study of this kind have been well established by King.²

The plant food of the soil, it is well understood, only has access to the absorbent organs of the plant when presented in a proper soluble or semi-soluble form in connection with water. From a chemical standpoint, in connection with the subject under discussion, the movement of water in the soil should be considered in connection, not alone with its power of dissolving plant foods, but with especial reference to its power of carrying them not only away from the reach of the roots of the plant, but even out of the field and into the streams and rivers and eventually into the sea. For our present purpose, therefore, we have only need to examine lysimetric observations for the

¹ "Some Physical Properties of Soils," U. S. Weather Bureau, Bulletin No. 4.

² Ninth Annual Report of the Wisconsin Experiment Station, p. 129, *et seq.*

purpose of determining the kinds of plant food which are most exposed to waste. It is not my purpose to take your time here with a vast array of figures, but I desire only to call your attention to the fact that of the chief plant foods, potash and the nitrates are the ones which are most exposed to loss.

The earliest systematic investigations of the quantity and composition of drainage were commenced at the Rothamsted Station by Lawes and Gilbert¹, in 1870. Lysimeters were constructed for the collection of the drainage water from thirty, forty, and sixty inches depth of soil, respectively, the soil and subsoil being kept in the natural state of aggregation.

Lawes and Gilbert call attention to the fact that, probably, at the Rothamsted Station, not more than five pounds of nitrogen are secured per acre each year from the atmosphere and the rain-water, while the average loss of nitrogen through the drainage water is over thirty pounds per acre. The quantity, of course, varies with the amount of rain-fall and the activity of nitrification. They speak of the possible exaggeration of the loss of nitrogen on account of the fact that the air had access to the soil both from below and above and therefore the process of nitrification where the lysimeters were placed might have been intensified.

Among the latest researches on this subject are those of Deherain.² It is pointed out by this author that the character of the crop grown upon the cultivated field has much to do with the determination of the loss of nitrogen per acre. Those crops which require an immense amount of moisture for their growth, such as the sugar beet, would tend thereby to prevent the loss of nitrogen in the drainage waters, the nitrates being stored in the beet instead of being given up to percolation. In general, it may be said that it is the quantity of the drainage water rather than its richness in nitrates which determines the total loss due to percolation, and from this it may be inferred that the loss by drainage is directly proportional to the rain-fall and inversely proportional to the magnitude of the harvest. The season at which the greatest loss takes place is also, there-

¹ *Jour. Roy. Agric. Soc.*, 17, 241-79 and 311-50; 18, 1-71.

² *Annales Agronomiques*, February 25, 1893, pp 65, et seq.

fore, the one in which the growth of the plant is the least vigorous, provided that the vigor of nitrification and quantity of rain-fall remain the same. When plants grow vigorously and when they occupy the soil for a long time, the losses due to drainage are reduced to a minimum. On the other hand, with plants which rapidly ripen, so that the harvest follows soon after the sowing, the losses are greater. The farmer, therefore, who suffers a failure of his crop, not only loses from the smallness of the harvest, but also by the percolation of the water through the soil. For this reason, it is obvious that leaving fields fallow is a very dangerous proceeding. Deherain found that fallow fields during the season lost as high as fifty kilograms of nitrogen per hectare, corresponding to 330 kilograms of nitrate of soda, worth seventy-six francs. These figures show plainly the magnitude of the losses which take place in the one item of nitrogen alone, due to the percolation of rain-water through the soil.

In this connection it may be of interest again to refer to the favorable action of lime in a great many soils in regard to its power of increasing the ability of a soil to hold the soluble plant foods against their removal by water. This favorable action is particularly manifested in many soils in the power of lime to increase their capacity for holding potash.

Warington explains this action of the lime salts, especially the carbonate, by suggesting that by combining with the acids of certain salts, as the carbonates, sulphates, chlorides, and nitrates, they allow the bases of these salts to unite with the hydrated metallic oxides. The carbonate of lime also converts the soluble acid phosphates, applied in manure, to the sparingly soluble calcium phosphates, which, as they gradually enter into solution are converted into ferric and aluminic phosphates. An admirable description of the absorptive power of soils has been given by Warington¹ and many other authors have also discussed this matter in detail.

We can see from the data given above how water continually acts upon a soil in the removal of certain soluble plant foods. It might be inferred from this that all arable soils exposed con-

¹ "Practice with Science," 2.

tinually to rains would soon be exhausted of all valuable, soluble plant food. But it has also been pointed out how certain constituents of the soil have a faculty of absorbing and retaining materials which are soluble in water under ordinary conditions. It must not be forgotten also that the rain-water which descends upon the earth is not pure. Rain-water brings to the earth a certain amount of valuable plant food. Not only does it absorb and hold in solution ammonia and nitric acid, which may be formed by the electrical discharges in the air, but it also collects and brings to the surface of the earth vast quantities of meteoric dust containing valuable fertilizing principles. Thus we have constantly entering the soil water which contains more or less of the materials necessary to plant growth. Even the drainage waters, which leave an arable field, may not reach the sea without giving up much of this material. The drainage waters in passing underneath the earth's surface take devious courses and are often brought near to the surface again or are poured upon soils which are quite different in their texture from those furnishing the materials in solution. Sterry Hunt¹ has pointed out how such waters sooner or later come upon permeable strata by which they are absorbed and in their subterranean circulation undergo important changes. Especially when these waters reach argillaceous strata their content of neutral, soluble salts may suffer great changes. Such waters charged with organic and mineral materials contain usually large amounts of potassium salts and notable quantities of silica and phosphates, and in many cases ammoniated salts, and nitrites or nitrates.

The experiments of Way, Voelcker, and others have shown that in contact with argillaceous sediments these waters give up their potash, ammonia, silica, phosphoric acid and organic matter, which remain in combination with the soil; on the other hand, soda, magnesia, sulphuric acid and chlorine are not removed from the drainage waters. Eichorn attributes this power of selective absorption in the soil chiefly to the action of hydrated double aluminum silicates, and supposes that the process is one of double exchange, equivalents of lime or soda being given up for the potash retained. By this power of

¹ "Chemical and Geological Essays," 95.

selective absorption the mineral matters required for the growth of plants tend to be retained in most soils, while those not required for the growth of plants are removed. Nevertheless, much of the valuable mineral material in solution must escape absorption and finally find its way into the streams, rivers, and seas.

From the foregoing summary of the methods of waste of plant food it has been seen that in spite of all the precautions of the farmer and the chemist, and in spite of the selective absorption of the soil, immense quantities of valuable plant food are carried into the sea, where apparently they are lost to agriculture forever. But this is only an apparent loss. The economies of nature are so happily adjusted as to provide a means of gradually returning in some form or other to the power of the farmer the plant food which has been apparently destroyed. It is true that this return will probably not be to the locality where the waste originally occurred, and it may not take place until after the lapse of thousands of years, but this is of no consequence. Provided arable lands in general receive in some way and at some time a certain return for the plant food removed, it is entirely immaterial whether this be the original plant food removed or other equally as good.

The sea is the great sorting ground into which all this waste material is poured. The roller processes of nature, like the mills of the gods, grind exceedingly slow and small, and the sea becomes the bolting cloth by which the products of milling are separated and sorted out. As soon as this waste material is poured into the sea, the process of sorting at once begins. The carbonate of lime becomes deposited in vast layers, or by organic life is transformed into immense coral formations or into shells. Phosphoric acid is likewise sifted out into phosphatic deposits or passes into the organic life of the sea. Even the potash, soluble as it is, becomes collected into mineral aggregates or passes into animal or vegetable growth. All these valuable materials are thus conserved and put into a shape in which they may be returned sooner or later, to the use of man. In the great cosmic economy there is no such thing as escape from usefulness of any valuable material.

Sterry Hunt¹ has called especial attention to this sifting and sorting power of water and the important part it plays in the formation of crystalline rocks. "Igneous fusion," he says, "destroys the mineral species of the crystalline and brings them back as nearly as possible to the great primary and undifferentiated material. This is the great destroyer and disorganizer or mineral as well as of organic matter. Subterranean heat in our time acting on buried aqueous sediments destroys carbonates, sulphates, and chlorides, with the evolution of acidic gases and the generation of basic silicates and thus repeats in miniature the conditions of the anteneptunian chaos.

"On the other hand each mass of cooling igneous rock in contact of water begins anew the formative process. The hydrated amorphous product palagonite, is, if we may be allowed the expression, a sort of silicated protoplasm and by its differentiation yields to the solvent action of water, the crystalline silicates which are the constituent elements of the crenitic rocks, leaving at the same time a more basic residuum abounding in magnesia and iron oxide and soluble not by crenitic but sub-aerial action."

Let me call attention, for a few moments, to some of the more important ways, pointed out through the researches of agricultural chemists, in which these waste products are restored. We are inclined to look upon the sea as devoid of vegetable growth, but the gardens of the sea are no less fully stocked with economic plants than the gardens of the land. The sea-weeds of all genera and species are constantly separating valuable materials from the waters of the ocean and placing them again in organic form. Many years ago Forchhammer² pointed out the agricultural value of certain fucoids. Many chemists have contributed important data in regard to the composition of these bodies. Jenkins³ gives analyses of several varieties of sea-weed, showing that in the green state it is quite equal to stall manure. The farmers are said to pay as high as five cents a bushel for it. Goessmann⁴ also gives analyses of several varieties of sea-weed.

¹ *Mineral Physiology and Physiography*, 188.

² *J. prakt. Chem.*, 1st Series, 38, 388.

³ *Annual Report, Conn. State Exp't. Sta.*, 1890, 72.

⁴ *Annual Report, Mass. State Exp't. Sta.*, 1887, 223.

We are indebted, however, to the reports of Wheeler and Hartwell' for the fullest and most systematic discussion of the agricultural value of sea-weeds which has been published. Their interesting and elaborate report was published in January, 1893. Those who are interested in the details of this work can find all known publications on the subject properly arranged, classified, and studied in the publication mentioned. We learn from this publication that sea-weed was used as a fertilizer as early as the fourth century, and its importance for this purpose has been recognized more and more in modern days, especially since chemical investigations have shown the great value of the food materials contained therein.

To show the commercial importance of sea-weed as a fertilizer, it is only necessary to call attention to the fact that in 1885 its value for use as fertilizer in the State of Rhode Island was \$65,044, while the value of all other commercial fertilizers was only \$164,133. While sea-weed, in a sense, can only be successfully applied to littoral agriculture, yet the extent of agricultural lands bordering on the sea is so great as to render the commercial importance of the matter of the highest degree of interest.

It is not my intention here to enter into the discussion of the methods of preparing the sea-weed, the times at which it should be gathered and the best means of applying it to the soil; these matters are all thoroughly discussed by Wheeler and Hartwell in the publication mentioned. As an instance of the value of sea-weed at a point far removed from the Rhode Island coast, I may be permitted to say that near the mouth of the Caloosahatchee river, at the town of Ft. Meyers. I saw the most happy effects produced in intensive culture by the application of sea-weed alone to the sandy soils bordering on this arm of the sea. Dr. Washburn, of the Florida Experiment Station, was conducting the experiments to which I refer and he spoke in the highest terms of the value of the sea-weed in his work. Thousands of tons of this sea-weed are allowed to go to waste annually along these shores, simply because the agriculturist has not been informed in regard to its fertilizing value.

There are many other uses for sea-weed besides the agricul-

¹ Rhode Island Exp't. Sta. Bull. 21.

tural one but in these we are not much interested, except incidentally. Many of the varieties of sea-grass are used for filling mattresses, cushions, etc. Other varieties are burned and their ashes used for the manufacture of soda, iodine, and bromine. The gelatinous portions of sea-weeds become exceedingly hard and elastic upon being dried and have been moulded into various forms as substitutes for horn and shells in making handles for knives, files, and other tools. In the Techno-Chemical receipt book, on page 177, may be found receipts for making artificial ebony from the charcoal obtained from sea-weeds; also for making leather, soap, and glue. For the latter purpose the plants are dried and powdered, extracted with warm water, with or without the addition of alcohol. The solution is allowed to settle at a temperature of 120° F. When cool it forms a jelly which is used for various purposes. The direction is then given for making transparent sea-weed leather, opaque sea-weed leather, sea-weed soap, and sea-weed glue.

No attempt can be made to give the quantities of sea-weed which are annually cast upon the shores of the different continents. Perhaps Rhode Island is no more favored in this respect than any other locality and we have seen the value of the sea-weed which was gathered for agricultural purposes in that State alone. The amount gathered represents only a very small fraction of the amount which was thrown upon the shores. It is easy, therefore, to conclude that the quantities of nitrogen, phosphoric acids and potash annually removed from the seas by the plants living therein are no less great in magnitude than those removed from the land by crops and plants of all kinds.

But sea-weed and other vegetable products of the sea are not the only vehicles in which the plant food in solution in the waters of the ocean may be returned to the uses of man. The animal life of the ocean is not less important than that of the land. In the animal economy of the ocean are gathered, therefore, immense quantities of valuable food material which are thus placed in a condition to be at least in part restored in the form of food. Relatively, phosphoric acid and nitrogen are restored in much greater quantities than potash. The composition of fish in general shows that relatively larger quantities of

phosphoric acid and nitrogen are found than of fat and potash. The chemical composition of the nutritive portion of fishes has been thoroughly investigated by Atwater.¹

The percentage of phosphoric acid in the flesh of American fishes, in its fresh state, is about one-half of one per cent. In one instance, that of smelt, Atwater found, 0.81 per cent. in the flesh of the fish. In the water-free substance of the flesh the percentage of phosphoric acid in round numbers is 2.5. In the case of the smelt above mentioned it amounted to 5.49 per cent. When it is considered that the bones and other refuse of the fish presumably richer in phosphoric acid than the flesh, were not included in this investigation, the quantity of phosphoric acid in fish is distinctly brought to view.

The quantity of albuminoids in the water-free substance of the flesh of fish is enormously high as compared with that of ordinary foods. In round numbers it may be said to be about 75 per cent. of the total water-free substance. In some cases the albuminous matter, or in other words the protein, makes up almost the whole of the water-free substance as in the case of a brook trout, quoted by Atwater, in which the percentage of protein in the dry flesh was 93.25; and of a perch in which it was 93.33; and of a sea bass in which it was 95.88; and a red snapper in which it was 95.38, and others in which even a higher percentage was reported.

It is thus seen that the ordinary fishes of the ocean collect, especially the two great elements of plant food, phosphorus, and nitrogen.

Oysters and other shell fishes collect not only large quantities of phosphorus and nitrogen, but also larger quantities of carbonate of lime. As has been intimated in another place, it is entirely probable that in earlier times when the sea was richer in phosphoric acid than at present, considerable quantities of phosphate of lime may have been secreted with the carbonate of lime in the shell. At the present time, however, the phosphate of lime has almost or quite disappeared from the matters of which shells are composed.

¹ The Chemical Composition and Nutritive Values of Food Fish and Aquatic Vertebrates, by W. O. Atwater. Report of the U. S. Commissioner of Fish and Fisheries, 1888, 679-868.

While the art of fishing is practiced chiefly for the purpose of gaining human food, yet in many large fishing districts the fish waste becomes valuable fertilizing material. Some kinds of fish, as the menhaden, are, however, collected chiefly for their fertilizing value. The use of fish for fertilizing purposes is not new. A most interesting description of the use of agricultural fertilizers by the American Indians is given by Goode.¹ As long ago as 1875 the value of the nitrogen derived from the menhaden was estimated to be about two million dollars. In the year 1878 it is estimated that 200,000 tons of menhaden fish were captured between Cape Henry and the Bay of Fundy. The oil is first extracted from the fish for commercial purposes and afterward the residue is dried and ground and sold to farmers and fertilizer manufacturers. For a complete history of the menhaden the articles of Prof. G. Brown Goode, in the report of the U. S. Commissioner of Fish and Fisheries for 1877 and 1879, may be consulted.

The honor of teaching the American colonists the use of artificial fertilizers belongs, without doubt, to an Indian named Squanto. In Governor Bradford's "History of Plimouth Plantation" is given an account of the early agricultural experiences of the Plymouth colonists. In April, 1621, at the close of the first long dreary winter "they (as many as were able) began to plant their corne, in which service Squanto (an Indian) stood them in great stead, showing them both ye manner how to set it, and after how to dress and tend it. Also he tould them, axcepte they got fish and set with it (in these old grounds) it would come to nothing; and he showed them yt in ye middle of Aprili, they should have store enough come up ye brooke by which they begane to build and taught them how to take it."²

Another account mentioned by Goode of the practice of the Indians in this respect may be found in George Mourt's "Relation or Journal of the Beginning and Proceedings of the English Plantation settled at Plimouth in New England, by certain English Adventurers, both merchants and others, London, 1622." "We set the last spring some twenty acres of Indian corn, and

¹ American Naturalist, 14, July, 1880, No. 7., 473, *et seq.*

² Coll. Mass. Hist. Soc., 4th Series, 3, 100, 1856.

sowed some six acres of barley and pease, and, according to the manner of the Indians, we manured our ground with herrings, or rather shads, which we have in great abundance and take with great ease at our doors. Our corn did prove well, and God be praised, we had a good increase of Indian corn, and our barley indifferent good."¹

Thomas Morton, in his "New England Canaan," London, 1632, wrote of Virginia: "There is a fish (by some called shadds, by some, allizes,) that at the spring of the yeare passe up the rivers to spawn in the pond, and are taken in such multitudes in every river that hath a pond at the end that the inhabitants dounge their ground with them. You may see in one township a hundred acres together, set with these fish, every acre taking 1,000 of them, and an acre thus dressed will produce and yield so much corn as three acres without fish; and (least any Virginea man would inferre hereupon that the ground of New England was barren, because they use more fish in setting their corne, I desire them to be remembered, the cause is plaine in Virginea) they have it not to sett. But this practice is onely for the Indian maize (which must be set by hands), not for English grain; and this is, therefore, a commodity there."

The following amusing study quoted by Goode is taken from the records of the town of Ipswich, May 11, 1644:

"It is ordered that all the doggs for the space of three weeks from the publishing hereof, shall have one legg tyed up, and if such a dog shall break loose and be found doing harm the owner of the dogg shall pay damage. If a man refuse to tye up his dogg's legg, and hee bee found scraping up fish in a cornfield, the owner thereof shall pay twelve pence damage beside whatever damage the dogg doth. But if any fish their house lotts and receive damage by doggs, the owners of these house lotts shall bear the damage themselves."

The practice of using fish, therefore, for fertilizing purposes, is many centuries old, but until recent years the farmers residing along the coast were the only ones who received any benefit therefrom; but since the more careful scientific study of the value of fish fertilization, the nitrogenous elements taken from

¹ Coll. Mass. Hist. Soc., 2nd Series, 9, 1872, 60.

the sea by the fish now find their way not only to the gardens and truck farms along the New England and New Jersey coasts but also to the wheat fields of Ohio and the cotton fields of North Carolina.

Conservation of Nitrogen.—Attention has been called to the manner in which the nitrogen carried into the ocean by the waste of the land is returned in great part through the marine, vegetable, and animal life. Immense quantities of waste nitrogen, however, are further secured, both from sea and land, by the various genera of birds. The well-known habits of birds in congregating in rookeries during the nights, and at certain seasons of the year tends to bring into a common receptacle the nitrogenous matters which they have gathered and which are deposited in their excrement and in the decay of their bodies. The feathers of birds are particularly rich in nitrogen, and the nitrogenous content of the flesh of fowls is also high. The decay therefore, of remains of birds, especially if it take place largely excluded from the leaching of water, tends to accumulate vast deposits of nitrogenous matter. If the conditions in such deposits are favorable to the processes of nitrification, the whole of the nitrogen, or at least the larger part of it, which has been collected in this débris, becomes finally converted into nitric acid and is found combined with appropriate bases as deposits of nitrates. The nitrates of the guano deposits and of the deposits in caves arise in this way. If these deposits are subject to moderate leaching the nitrate may become infiltrated into the surrounding soil, making it very rich in this form of nitrogen. The beds and surrounding soils of caves are often found highly impregnated with nitrates.

While for our purpose, deposits of nitrates only are to be considered which are of sufficient value to bear transportation, yet much interest attaches to the formation of nitrates in the soil even when they are not of commercial importance.

In many soils of tropical regions not subject to heavy rain-falls, the accumulation of these nitrates is very great. Müntz and Marciano¹ have investigated many of these soils to which attention was called first by Humboldt and Boussingault.

¹ *Compt. rend.*, 101, 1885, 65, et seq.

They state that these soils are incomparably more rich in nitrates than the most fertile soils of Europe. The samples which they examined were collected from different parts of Venezuela and from the valleys of the Orinoco as well as on the shore of the Sea of Antilles. The nitrated soils are very abundant in this region of South America where they cover large surfaces. Their composition is variable, but in all of them carbonate and phosphate of lime are met with and organic nitrogenous material. The nitric acid is found always combined with lime. In some of the soils as high as thirty per cent. of nitrate of lime have been found. Nitrification of organic material takes place very rapidly the year round in this tropical region. These nitrated soils are everywhere abundant around caves, as described by Humboldt, caves which serve as the refuge of birds and bats. The nitrogenous matters, which come from the decay of the remains of these animals, form true deposits of guano which are gradually spread around, and which, in contact with the limestone and with access of air, suffer complete nitrification with the fixation of the nitric acid by the lime.

Large quantities of this guano are also due to the débris of insects, fragments of elytra, scales of the wings of butterflies, etc., which are brought together in those places by the millions of cubic meters. The nitrification, which takes place in these deposits, has been found to extend its products to a distance of several kilometers through the soil. In some places the quantity of the nitrate of lime is so great in the soils that they are converted into a plastic paste by this deliquescent salt.

It is suggested by the authors that the co-existence of the nitrate and phosphate of lime is sufficient in all cases to demonstrate the organic origin of the nitric acid. It would not be possible to attribute such an origin to the nitrate present in these soils if it could not be determined that it was thus associated with phosphate and other remains, the last witnesses of a former animal life.

As a result of the observations of Müntz and Marcano, they conclude that it is not proper to accredit to the electrical discharges in the atmosphere the origin of the nitric acid forming

these deposits although they admit primarily the source of the nitric acid may have been due to electricity, but that it first was passed through the organism of the plant and thence into that of the animal whence it is accumulated in the deposits referred to.

The theory of Müntz and Marcano in regard to the nitrates of soils, especially in the neighborhood of caves, is probably a correct one, but there are many objections to accepting it to explain the great deposits of nitrate of soda which occur in many parts of Chile. Another point, which must be considered also, is this: That the processes of nitrification can not now be considered as going on with the same vigor as formerly. Some moisture is necessary to nitrification, as the nitrifying ferment does not act in perfectly dry soil, and in many localities in Chile where the nitrates are found it is too dry to suppose that any active nitrification could now take place.

The existence of these nitrate deposits has long been known.¹ The old Indian laws originally prohibited the collection of the salt, but nevertheless it was secretly collected and sold. Up to the year 1821, soda saltpeter was not known in Europe except as a laboratory product. About this time the naturalist, Mariano de Rivero, found on the Pacific coast, in the Province of Tarapacá, immense new deposits of the salt. Later the salt was found in equal abundance in the Territory of Antofagasta and further to the south in the desert of Atacama, which forms the Department of Taltal.

At the present time the collection and export of saltpeter from Chile is a business of great importance. The largest export which has ever taken place in one year was in 1890, when the amount exported was 927,290,430 kilograms; of this quantity 642,506,985 kilograms were sent to England and 86,124,870 kilograms to the United States. Since that time the imports of this salt into the United States have largely increased.

According to Pissis² these deposits are of very ancient origin. This geologist is of the opinion that the nitrate deposits are the result of the decomposition of feldspathic rocks; the bases thus

¹ A most interesting article on the subject may be found in *Jour. Roy. Agric. Soc.*, 1852, 13, 349, et seq.

² Fuchs and De Launy, *Traité des Gîtes Minéraux*, 1893, 1, 425.

produced gradually becoming united with the nitric acid provided from the air.

According to the theory of Nöllner¹ the deposits are of more modern origin and due to the decomposition of marine vegetation. Continuous solution of soils beneath the sea gives rise to the formation of great lakes of saturated water, in which occurs the development of much marine vegetation. On the evaporation of this water, due to geologic isolation, the decomposition of nitrogenous organic matter causes generation of nitric acid, which, coming in contact with the calcareous rocks, attacks them, forming nitrate of calcium, which, in presence of sulphate of sodium, gives rise to a double decomposition into nitrate of soda and sulphate of calcium.

The fact that iodine is found in greater or less quantity in Chile saltpeter is one of the chief supports of this hypothesis of marine origin, inasmuch as iodine is always found in sea plants and not in terrestrial plants. Further than this, it must be taken into consideration that these deposits of nitrate of soda contain neither shells nor fossils, nor do they contain any phosphate of lime. The theory, therefore, that they were due to animal origin is scarcely tenable.

Lately extensive nitrate deposits have been discovered in the U. S. of Columbia.² These deposits have been found extending over thirty square miles and vary in thickness from one to ten feet. The visible supply is estimated at 7,372,800,000 tons, containing from 1.0 to 13.5 per cent. of nitrate. The deposits consist of a mixture of nitrate of soda, chloride of soda and sulphate of calcium, sulphate of alumina, and insoluble silica. It is thought that the amount of these deposits will almost equal those in Chile and Peru.

Phosphatic Deposits.—Gautier³ calls attention to the fact that the oldest phosphates are met with in the igneous rocks, such as basalt, trachyte, etc., and even in granite and gneiss. It is from these inorganic sources, therefore, that all phosphatic plant food must have been drawn. In the second order in age

¹ El Salitre de Chile, René F. Le Peuvre y Arturo Dagino, 1893, 12.

² Bureau of American Republics, *Monthly Bulletin*, December, 1893, 18, et seq.

³ *Compt. rend.*, 116, 1271, 6.

Gautier places the phosphates of hydro-mineral origin. This class not only embraces the crystalline apatites but also those phosphates of later formation, formed from hot mineral waters in the jurassic, cretaceous, and tertiary deposits.

These deposits are not directly suited to nourish plants.

The third group of phosphates in order of age and assimilability embraces the true phosphorites containing generally some organic matter. They are all of organic origin. In caves where animal remains are deposited there is an accumulation of nitrates and phosphates.

Not only do the bones of animals furnish phosphates, but they are also formed in considerable quantities by the decomposition of substituted glycerides such as lecithin.

The ammonia produced by the nitrification of the albuminoid bodies combines with the free phosphoric acid thus produced, forming ammonium or diammonium phosphates.

The presence of ammonium phosphates in guanos was first noticed by Chevreul more than half a century ago.

If such deposits overlay a pervious stratum of calcium carbonate, such as chalk, and are subject to leaching, a double decomposition takes place as the lye percolates through the chalk. Acid calcium phosphate and ammonium carbonate are produced. By further nitrification the latter becomes finally converted into calcium nitrate. In like manner aluminum phosphates are formed by the action of decomposing organic matter on clay.

Davidson¹ explains the origin of the Florida phosphates by suggesting that they arose chiefly through the influx of animals driven southward by the glacial period. According to his supposition the waters of the ocean, during the cenozoic period contained more phosphorus than at the present time. The waters of the ocean over Florida were shallow and the shell fish existing therein may have secreted phosphate as well as carbonate of lime. This supposition is supported by an analysis of a shell of *lingula ovalis*, quoted by Dana, in which there were 85.79 per cent. of lime phosphate. In these waters were also many fishes of all kinds and their débris served to increase the

¹ *Engineering and Mining Journal*, quoted in the "Phosphates of America," by Wyatt, 66, et seq.

amount of this substance. As the land emerged from the sea came the great glacial epoch driving all terrestrial animals southward. There was therefore a great mammal horde in the swamps and estuaries of Florida. The bones of these animals contributed largely to the phosphatic deposits. In addition to this, the shallow sea contained innumerable sharks, manatees, whales and other inhabitants of tropical waters, and the remains of these animals added to the phosphatic store.

While these changes were taking place in the quaternary period, the Florida peninsula was gradually rising and as soon as it reached a considerable height, the process of denudation by the action of water commenced. Then there was a subsidence and the peninsula again passed under the sea and was covered with successive layers of sand. The limestones during this process, had been leached by rain-water containing an excess of carbonic acid. In this way the limestones were gradually dissolved while the insoluble phosphate of lime was left in suspension. During this time the bones of the animals before mentioned by their decomposition added to the phosphate of lime present in the under lying strata, while some were transformed into fossils of phosphate of lime just as they are found to-day in vast quantities.

Wyatt¹ explains the phosphate deposits somewhat differently. According to him, during the miocene submergence there was deposited upon the upper eocene limestones, more especially in the cracks and fissures resulting from their drying up, a soft, finely disintegrated calcareous sediment or mud. The estuaries formed during this period were swarming with animal and vegetable life, and from this organic life the phosphates were formed by decomposition and metamorphism due to the gases and acids with which the waters were charged.

After the disappearance of the miocene sea there were great disturbances of the strata. Then followed the pliocene and tertiary periods and quaternary seas with their deposits and drifts of shells, sands, clays, marls, boulders and other transported materials, supervening in an era when there were great fluctuations of cold and heat.

¹ *Engineering and Mining Journal*, August 23, 1890.

By reason of these disturbances the masses of the phosphate deposits which had been infiltrated in the limestones became broken up and mingled with the other débris and were thus deposited in various mounds or depressions. The general result of the forces which have been briefly outlined, was the formation of boulders, phosphatic débris, etc. Wyatt therefore classifies the deposits as follows:

1. Original pockets or cavities in the limestone filled with hard and soft rock phosphates and débris.
2. Mounds or beaches, rolled up on the elevated points, and chiefly consisting of huge boulders of phosphate rock.
3. Drift or disintegrated rock, covering immense areas, chiefly in Polk and Hillsboro counties, and underlying Peace river and its tributaries.

N. H. Darton, of the U. S. Geological Survey, ascribes the phosphate beds of Florida to the transformation of guano.¹ According to this author two processes of decomposition have taken place; one of these is the more or less complete replacement of the carbonate by the phosphate of lime; the other is a general stalactitic coating of phosphatic material. Darton further calls attention to the relation of the distribution of the phosphate deposits as affecting the theory of their origin, but does not find any peculiar significance in the restriction of these deposits to the western ridge of the Florida peninsula.

As this region evidently constituted a long, narrow peninsula during early miocene times it is a reasonable, tentative hypothesis that during this period guanos were deposited from which was derived the material for the phosphatization of the limestone either at the same time or soon after.

Darton closes his paper by saying that the phosphate deposits in Florida will require careful, detailed geologic exploration before their relations and history will be fully understood.

According to Dr. N. A. Pratt the rock or boulder phosphate had its immediate origin in animal life and the phosphate boulder is a true fossil. He supposes the existence of some species in former times in which the shell excreted was chiefly phosphate of lime. The fossil boulder, therefore,

¹ *Amer. Jour. of Science*, 41, February, 1891.

becomes the remains of a huge foraminifer which had identical composition in its skeleton with true bone deposits or of organic matter.

Perhaps the most complete exposition of the theory of the recovery of waste phosphates, with especial reference to their deposition in Florida, has been given by Eldridge,¹ of the U. S. Geological Survey. Eldridge calls attention to the universal presence of phosphates in sea water and to the probability that in earlier times, as during the miocene and eocene geologic periods, the waters of the ocean contained a great deal more phosphate in solution than at the present time. He cites the observations of Bischof, which show the solubility of different phosphates in waters saturated with carbon dioxide. According to these observations apatite is the most insoluble form of lime phosphate, while artificial basic slag phosphate is the most soluble. Among the very soluble phosphates, however, are the bones of animals, both fresh and old. Burnt bones, however, are more soluble than bones still containing organic matter. Not only are the organic phosphates extremely soluble in water saturated with carbon dioxide but also in water which contains common salt or chloride of ammonium. The presence of large quantities of common salt in sea water would, therefore, tend to increase its power of absorbing lime phosphates of organic origin. It is not at all incredible, therefore, to suppose that at some remote period the waters of the ocean, as indicated by these theories, were much more highly charged with phosphates than at the present time.

According to Eldridge, the formation of the hard rock and soft phosphates may be ascribed to three periods: First, that in which the primary rock was formed; second, that of secondary deposition in the cavities of the primary rock; third, that in which the deposits thus formed were broken up and the resulting fragments and comminuted material were redeposited as they now occur.

"The first of these stages began probably not later than the close of the older miocene, and within the eocene area it may

¹ A preliminary sketch of the phosphates of Florida. By Geo. H. Eldridge, author's edition, 1892, 18, *et seq.*

have begun much earlier. Whether the primary phosphate resulted from a superficial and heavy deposit of soluble guanos, covering the limestones, or from the concentration of phosphate of lime already widely and uniformly distributed throughout the mass of the original rock, or from both, is a difficult question. In any event, the evidence indicates the effect of the percolation of surface-waters, highly charged with carbonic and earth-acids, and thus enabled to carry down into the mass of the limestone dissolved phosphate of lime, to be redeposited under conditions favorable to its separation. Such conditions might have been brought about by the simple interchange of bases between the phosphate and carbonate of lime thus brought together, or by the lowering of the solvent power of the waters through loss of carbonic acid. The latter would happen whenever the acid was required for the solution of additional carbonate of lime, or when, through aeration, it should escape from the water. The zone of phosphate-deposition was evidently one of double concentration, resulting from the removal of the soluble carbonate thus raising the percentage of the less soluble phosphate, and from the acquirement of additional phosphate of lime from the overlying portions of the deposit."

"The thickness of the zone of phosphatization in the eocene area is unknown, but it is doubtful if it was over twenty feet. In the miocene area the depth has been proved from the phosphates *in situ* to have been between six and twelve feet."

The deposits of the secondary origin, according to Eldridge, are due chiefly to sedimentation, although some of them may have been due to precipitation from water. This secondary deposition was kept up for a long period, until stopped by some climatic or geologic change. The deposits of phosphates thus formed in the Florida peninsula are remarkably free from iron and aluminum, in comparison with many of the phosphates of the West Indies.

The third period in the genesis of the hard-rock deposits embraces the period of formation of the original deposits and their transportation and storage as they are found at the present time. The geologic time at which this occurred is somewhat uncertain but it was probably during the last submergence of the peninsula.

In all cases the peculiar formation of the Florida limestone must be considered. This limestone is extremely porous and, therefore, easily penetrated by the waters of percolation. A good illustration of this is seen on the southwestern and southern edges of Lake Okeechobee. In following down a drainage canal which had been cut into the southwest shore of the lake I saw the edge of the basin, which is composed of this porous material. The appearance of the limestone would indicate that large portions of it had already given way to the process of solution. The remaining portions were extremely friable, easily crushed, and much of it could be removed by the ordinary dredging machines. Such a limestone as this is peculiarly suited to the accumulation of phosphatic materials, due to the percolation of the water containing them. The solution of the limestone and consequent deposit of the phosphate of lime is easily understood when the character of this limestone is considered.

Shaler, as quoted by Eldridge in the work already referred to, refers to this characteristic of the limestone and says that the best conditions for the accumulation of valuable deposits of lime phosphate in residual *débris* appear to occur where the phosphatic lime marls are of a rather soft character; the separate beds having no such solidity as will resist the percolation of water through innumerable incipient joints such as commonly pervade stratified materials, even when they are of a very soft nature.

Eldridge is also of the opinion that the remains of birds are not sufficient to account for the whole of the phosphatic deposits in Florida. He ascribes them to the joint action of the remains of birds, of land and marine animals and to the deposition of the phosphatic materials in the waters in the successive subsidences of the surface below the water line.¹

Potash Deposits.—In the foregoing pages I have tried to set clearly before you the different ways in which the waste of nitrogen and phosphoric acid has been recovered by nature in a form suitable for restoration to arable fields. In the case of potash, however, we have seen that this

¹ For an elaborate discussion of phosphate deposits consult *Giles Mineraux, par Fuchs et DeLaunay*, 309, *et seq.*

element is not restored by the processes already mentioned, in amounts proportionate to nitrogen and phosphorus. Potash salts, being extremely soluble, are likely to be held longest in solution. Some of them, of course, are recovered in the animal and vegetable life, of which we have spoken, but the great mass of potash carried into the sea still remains unaccounted for. The recovery of the waste of potash is chiefly secured by the isolation of sea waters containing large quantities of this salt and their subsequent evaporation. Such isolation of sea waters takes place by means of geologic changes in the level of the land and sea. In the raising of an area above the sea level there is almost certain to be an enclosure, of greater or less extent, of the sea water in the form of a lake. This enclosure may be complete or only partial, the enclosed water area being still in communication with the main body of the sea by means of small estuaries. If this body of water be exposed to rapid evaporation, as was doubtless the case in past geologic ages, there will be a continual influx of additional sea water through these estuaries to take the place of that evaporated. The waters may thus become more and more charged with saline constituents. Finally a point is reached in the evaporation when the less soluble of the saline constituents begin to be deposited. In this way the various formations of mineral matter, produced by the drying up of enclosed waters, take place.

The most extensive deposits of potash known are those in the neighborhood of Stassfurt, in Germany. The following description probably represents the method of formation of these deposits:¹

"The Stassfurt salt and potash deposits had their origin, thousands of years ago, in a sea or ocean, the waters of which gradually receded, leaving near the coast, lakes which still retained communication with the great ocean by means of small channels. In that part of Europe the climate was still tropical, and the waters of these lakes rapidly evaporated but were constantly replenished through these small channels connecting them with the main body. Decade after decade this continued, until by evaporation and crystallization, the various salts pres-

¹ Potash, Columbian Exposition, German Kali Works, 3-4.

ent in the sea water were deposited in solid form. The less soluble material, such as sulphate of lime or 'anhydrite,' solidified first and formed the lowest stratum. Then came common rock salt with a slowly thickening layer which ultimately reached 3000 feet, and is estimated to have been 13,000 years in formation. This rock salt deposit is interspersed with lamellar deposits of 'anhydrite,' which gradually diminish towards the top and are finally replaced by the mineral 'polyhalite,' which is composed of sulphate of lime, sulphate of potash, and sulphate of magnesia. The situation in which this polyhalite predominates is called the 'polyhalite region' and after it comes the 'kieserite region,' in which, between the rock salt strata, kieserite (sulphate of magnesia) is imbedded. Above the kieserite lies the 'potash region,' consisting mainly of deposits of carnallite, a mineral compound of muriate of potash and chloride of magnesia. The carnallite deposit is from 50 to 130 feet thick and yields the most important of the crude potash salts and that from which are manufactured most of the concentrated articles, including muriate of potash."

"Overlying this region is a layer of impervious clay which acts as a water-tight roof to protect and preserve the very soluble potash and magnesia salts, which, had it not been for the very protection of this overlying stratum, would have been long ages ago washed away and lost by the action of the water percolating from above. Above this clay roof is a stratum, of varying thickness of anhydrite, (sulphate of lime,) and still above this a second salt deposit, probably formed under more recent climatic and atmospheric influences or possibly by chemical changes in dissolving and subsequent precipitation. This salt deposit contains ninety-eight per cent. (often more) of pure salt, a degree of purity rarely elsewhere found. Finally, above this are strata of gypsum, tenacious clay, sand, and limestone, which crop out at the surface."

"The perpendicular distance from the lowest to the upper surface of the Stassfurt salt deposits is about 5000 feet (a little less than a mile), while the horizontal extent of the bed is from the Harz Mountains to the Elbe River in one direction, and from the city of Magdeburg to the town of Bernburg in the other."

According to Fuchs and DeLauny¹ the saline formation near Stassfurt is situated at the bottom of a vast triassic deposit surrounding the city of Magdeburg. The quantity of sea water which evaporated to produce saline deposits of more than 500 meters in thickness must have been enormous and the rate of evaporation great. It appears that a temperature of 100° would have been quite necessary, acting for a long time, to produce this result.

These authors therefore admit that all the theories so far advanced to explain the magnitude of these deposits are attended with certain difficulties. What, for instance, could have caused a temperature of 100°? The most reasonable source of this high temperature must be sought for in the violent chemical action produced by the double decompositions of such vast quantities of salts of different kinds. There may also have been at the bottom of this basin some subterranean heat such as is found in certain localities where boric acid is deposited.

Whatever be the explanation of the source of the heat it will be admitted that at the end of the permian period there was thrown up to the northeast of the present saline deposits a ridge extending from Helgoland to Westphalia. This dam established throughout the whole of North Germany saline lagoons in which evaporation was at once established, and these lagoons were constantly fed from the sea.

There was then deposited by evaporation, first of all a layer of gypsum and afterwards rock salt, covering with a few exceptions the whole of the area of North Germany.

But around Stassfurt there occurred at this time geologic displacements, the saline basin was permanently closed and then by continued evaporation the more deliquescent salts, such as polyhalite, kieserite, and carnallite, were deposited.

These theories account with sufficient ease for the deposition of the saline masses, but do not explain why in those days the sea water was so rich in potash and why potash is not found in other localities where vast quantities of gypsum and common salt have been deposited. It may be that the rocks composing the shores of these lagoons were exceptionally rich in potash

¹ *Giles Minerals*, 429.

and that this salt was, therefore, in a certain degree, a local contribution to the products of concentration.

Through the ages of the past, the rich stores of plant food have been steadily removed from arable fields and apparently forever lost. But in point of fact no particle of it has been destroyed. Even the denitrifying ferments described by Springer, Gayon and Dupetit, and Muntz, reduce only to a lower stage of oxidation or restore to a gaseous form the nitric nitrogen on which alone vegetables can feed. But electricity, combustion, and the activity of certain anaerobic ferments herding in the rootlets of legumes and other orders of plants, are able to recover and again make available this loss.

Lately Winogradsky and Warington have shown that an organism can be grown in a sugar solution containing certain salts, and excluding all nitrogenous matter save the free nitrogen of the atmosphere, which is capable of oxidizing and assimilating this inert gas. In a solution containing 7 grams of sugar as high as 14 milligrams of nitrogen have been fixed.

Warington says in speaking of this phenomenon:

"That a vegetable organism should be able to acquire from the air the whole of the nitrogen which it needs, is certainly very remarkable and is an extraordinary fact both to the physiologist and the chemist."¹

The fact that a few million years may supervene before the particle that is carried off to-day as waste may return to organic life, shows the patience rather than the wastefulness of nature.

As a result of this general review of the migrations of plant food, the reassuring conclusion is reached that there is no danger whatever of the ultimate consumption or waste of the materials on which plants live. Circumscribed localities, through carelessness or ignorance, where once luxuriant crops grew, may become sterile, but the great source of supply is not exhausted. In fact, as the rocks decay and nitrifying organisms increase, the total store of plant food at the disposal of vegetation may continue to grow. When we join with this the fact that the skill of man in growing crops is rapidly increasing, we

¹ *Chem. News*, Oct. 13, 1893, 170.

find no danger ahead in respect of the quantity of human food which may be produced.

Only the novelist might be able, by the aid of an unfettered imagination, to say how many human beings the United States alone will be able to feed in comfort. With the aid of scientific agriculture, with the help of the agricultural chemist we may safely say that a thousand million people will not so crowd our means of subsistence as to make Malthus more than a pleasing theorist. As I pointed out in my vice-presidential address at Buffalo, the death of humanity is not to come from starvation but from freezing, and many a geologic epoch will come and go before this planet dies of cold.

A NEW FORM OF AIR-BATH.¹

BY EWALD SAUER, PH.D.

IN a recent article on the prevalent forms of air-baths, H. Petersen shows² conclusively that the designs ordinarily in vogue, whether made from copper or from aluminum,³ are far removed from the ideal of such an apparatus. The deficiencies are chiefly in the direction of variable temperature and insufficient ventilation for the purpose of rapidly removing the liberated steam. The use of jacketed air-baths, as Soxhlet's apparatus,⁴ while providing for constant temperature, limits the range of temperature to the boiling points of the liquids employed, and is subject also to limitations in size.

In order to obviate these difficulties, I have designed an air-bath, which while resembling externally the ordinary forms, differs from them in a few essential points. The main feature is the introduction of two bottoms which are connected with each other by several open tubes. These two bottoms are also joined together in the front and in the rear, while on the sides the space is open. A funnel-shaped opening in the center of the lower bottom allows the flame of an ordinary burner to freely

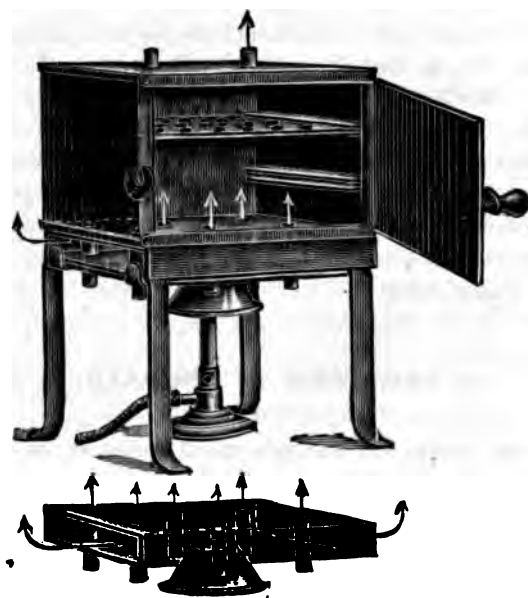
¹ Read before the Cincinnati Section, Oct. 14, 1893.

² *Ztschr. angew. Chem.*, 1892, 36.

³ *Ber. d. chem. Ges.*, 1892, 3637-40.

⁴ *Ztschr. angew. Chem.*, 1891, 363-68.

play on the lower surface of the upper or true bottom of the bath.



By means of this disposition the flame and the heated air current pass between the two bottoms about the series of connecting tubes, and issue on both sides. As a result, not only is the upper bottom heated, but also the series of tubes, while through the latter a current of hot air possessing the temperature of the upper bottom enters the interior of the bath. This hot current does double duty. In the first place it maintains a constant temperature in the bath; in the second, it effects a rapid removal of the aqueous vapor, which would be liberated as usual by the simple external heating.

That this device enables the chemist to secure the two desiderata of a constant temperature throughout the interior of the bath, and quick evaporation, is evident from the following tables of experimental results :

TABLE 1.

| Force of
Bunsen burner
flame. | Temperature upper
part of air-bath,
degrees. | Temperature lower
part of air-bath,
degrees. |
|-------------------------------------|--|--|
| 1 | 220 | 215 |
| $\frac{1}{2}$ | 128 | 127.5 |
| $\frac{1}{4}$ | 104.5 | 104.5 |
| $\frac{1}{8}$ | 83.5 | 83 |

The differences noted above are largely due to the different lengths of the mercury column of the thermometer enclosed in the heated space.

TABLE 2.

| Charge. | Temperature when empty. | Lowest temperature observed. | Temperature at close of evaporation. | Duration, minutes. | Grams of water evaporated. | Remarks. |
|--|-------------------------|------------------------------|--------------------------------------|--------------------|----------------------------|--|
| 5 grams asbestos and 10 grams water in a glass dish | 124.5° | 111° | 120° | 15 | 10 | Several experiments with uniform results showed that the location of the charge in the bath did not affect the time required. |
| | 118.5° | 111° | 115° | 40 | 10 | |
| 10 grams water in an aluminum dish.... | 124° | 111° | 114° | 14 | 10 | Several experiments showed conclusively that as soon as the water was completely evaporated the temperature returned rapidly to that indicated at the beginning. |
| | 103° | 96° | 102° | 14 | 10 | |
| 5 grams milk and 5 grams pumice stone in an aluminum dish.... | 100.5° | 92° | 95° | 12 | 5 | Slight darkening of the residue. |
| | 85° | 82° | 85° | 15 | 5 | |

The end of the operation is readily recognized by the fact that no moisture issues from the upper openings (indicated by an arrow in the diagrams), *i. e.*, a cold beaker held over the openings is not dimmed.

These new air-baths are manufactured from both copper and aluminum by Max Kaehler & Martini, 50 Wilhelmstrasse, Berlin.

THE CHEMICAL AND PHYSICAL INVESTIGATION OF SOILS.¹

By E. W. HILGARD, CALIFORNIA.

I DESIRE to place before this Congress, without going into analytical details which will be set forth in a special report to the Association of Official Chemists, the general results of my long-continued studies on direct soil examination by physical and chemical means that have led me to attach to such examinations a far greater practical importance than is now usually assigned to them by the consensus of opinion both in Europe and America.

I premise that I was led into these investigations more particularly as a consequence of my almost continuous residence in the newer, thinly-settled or unsettled portions of this country, where the question of the fitness of lands for general agriculture, and their special adaptations are burning questions, which are there constantly pressed upon the attention of whosoever occupies a public position in connection with agricultural colleges or experiment stations. My researches have, therefore, borne essentially on virgin soils, or at least such as had been cultivated only for a short time and had received not even incidental fertilization.

With material so different from that which in Europe and in the eastern United States have led most agricultural chemists to consider direct soil examination, and especially chemical soil analysis, as of little practical value, it is not surprising that I should have been led to conclusions differing somewhat widely from those commonly received; so that, while still agreeing that in the case of soils long fertilized, chemical analysis can give but little information as to the immediate producing power, I am satisfied that it can in the case of virgin soils be made of the most direct and vital use to the farmer and intending settler.

The substitute recommended for direct soil examination, after the sweeping condemnation of soil analysis some fifty years ago, was and still is, to put the question to the soil by cultivation and fertilization with the simples, potash, phosphoric acid, and nitrogen; and to deduce therefrom the needs of the soil. It

¹ Read before the World's Congress of Chemists, August 24, 1893.

goes without saying that this is but unpalatable advice to give to a settler in new regions; while even to the farmer in the older countries the carrying-out of a cogent experiment is by no means so easy a task as the precept implies. Moreover, the latter leaves room for great uncertainty in respect to seasonal differences; and the physical peculiarities of the soil are therein left totally out of consideration, although these are just as frequently in fault as the chemical composition, and the farmer is by no means usually to be credited with the ability to determine these points.

In my view, therefore, the examination of soils for the benefit of the agricultural population is one of the most needful, and in the newer states most urgent tasks set before the experiment stations; provided, of course, that the results can be successfully applied to practice.

My attention has from the outset been strongly drawn to the accuracy and certainty with which experienced farmers will, in a region familiar to them, judge of the quality and adaptations of land by its natural vegetation; more particularly by the forest growth. It is obvious that if we could interpret correctly the physical and chemical qualities of soils that have determined the choice of certain plants that occupy them as a result of secular co-adaptation by the survival of the fittest, we should have as definite and much more cogent data than can be supplied us at best by the brief culture experiments we can make. This thought suggested itself to me in noting the invariable recurrence of certain plants on soils showing obvious physical and chemical peculiarities, such as "stiffness" or "lightness" on the one hand, and richness in lime or humus on the other. I therefore determined to test the idea by actual, systematic examination of the soils in all their relations; and it is upon the results of this study, and of their *comparison with actual agricultural practice*, that my views in the premises are based. It need hardly be recalled to mind that, such relations once established, the conclusions flowing therefrom can be legitimately, and as experience shows, fruitfully, projected into cases in which the actual indications of natural vegetation are not available.

The first point requiring attention in such researches is, naturally, the observation of the soils in place, and the recording of all the peculiarities whether of occurrence, structure, derivation, depth, vegetation, local and general climate, and if possible, cultural experience. The taking of the sample to be examined must, of course, be made to conform to the particular conditions of each case, and not to arbitrarily prescribed precepts, above all things. All accidental, abnormal variations must be excluded by a proper selection of the localities, and by sampling the same soil in several places. That it is thus possible to obtain specimens correctly representing in all essentials a wide extent of country without excessive multiplication of samples, my experience has fully proved. The depth to which the "soil" sample should be taken is ordinarily the lower limit of coloration by humus; but should that depth exceed twelve inches, the presumable maximum depth of tillage, one sample should be taken to that depth only. The subsoil is what lies beneath that line of coloration; it is frequently advisable or necessary to sample the soil mass for each twelve inches down to six feet depth, since the nature of the subsoil is one of the most essential points to be observed in all cases.

The first operation I undertake upon any soil sample is to wash about ten grams of it in a beaker with a water current of definite velocity, while stirring actively with a rod. The residue of sand or gravel is examined, macroscopically and microscopically, for the determination of the chief constituent minerals and of their surface condition, whether sharp or much rounded. We thus gain at once a pretty definite estimate of its relations to its place of origin and of its parent rocks, and therefore of its probable general chemical character, it being presumable that the fine matter is of the same general nature as the coarse.

Then follows the "hand test" of the soil by crushing small lumps between the thumb and forefinger, dry at first; then, after wetting, observing the change of color on wetting, and then kneading, in order to test its contents of plastic clay.

The next step, logically, is the test of the relations of the soil to water or moisture. Since the perviousness to water coming from above is so variable according to the accidental condition

and the *modus operandi*, I prefer to determine, as more definite factors, the water capacity and the hygroscopic coefficient, both of which give very definite information in respect to the most essential physical properties of a soil.

In determining the *water capacity* it is quite essential to determine both the *maximum* and the *minimum*, and that in the lowest column of water with which one can operate; I place this at one cm. I use a cylindrical vessel with perforated bottom resembling the "test-lead sieve" of Plattner's blow-pipe chest, of twenty-five or fifty cc. capacity. This is filled with the fine earth, and after weighing placed in a shallow dish with a layer of water. Within about an hour it is saturated to the maximum capacity; it is then weighed, which gives the maximum. Then the wet soil is covered with soil, first air-dry, then with such as has been saturated with moisture, until its weight ceases to decrease by liquid absorption. The last weighing determines the minimum water capacity; the difference between the maximum and minimum indicates the greater or less height to which the soil will raise capillary, liquid water.

The *hygroscopic coefficient*, which contrary to prevailing doctrines I find to be of great importance to the welfare of plants in the arid regions, must be determined by exposing the soil to a fully saturated atmosphere for at least seven hours in a layer 1 mm. thick. Under such conditions, the amount absorbed remains practically the same within ordinary cellar temperatures, contrary to what (according to Knop's law) happens when the air is only partially saturated. We thus obtain a datum which bears a very definite ratio to the clay and humus contents of the soil and its drought-resisting qualities. But in order to obtain comparable results, the drying of the soil must be done at 200° C., for at 100° soils of high absorptive power will continue to lose moisture for weeks. The drying is therefore done in a paraffin bath. From the drying tube or bulb the quantities for the chemical determinations are weighed out.

In the question of the maximum size of grain to be admitted to the chemical analysis, I have also sought to determine by direct experiment the proper limit; instead of assuming an arbitrary one as is usually done, with the result that the chemists of each

country have adopted a different rule, and thus their work is rendered incapable of comparison. Thus the German stations have adopted a two mm. mesh for the fine earth sieve, while the French official rule is "one mesh to the millimeter," leaving the aperture an uncertain quantity because dependent upon the thickness of the wire used. As a matter of fact the aperture is about 0.75 mm. In this country one mm. clear aperture has been adopted by the majority of chemists. Thus it becomes impossible to compare with any degree of certainty the analyses of these different countries.

In 1872, having perfected my apparatus for mechanical soil analysis,¹ I caused an investigation of the question to be made by my assistant, Dr. R. H. Loughridge. The result (see *Am. J. Sci.*, January, 1874) was to show that in the very generalized soil worked upon, seventy-five per cent. of the dissolved soil ingredients was contained in the colloidal clay remaining suspended in water after twenty-four hours, in a column 200 mm. high; and that solution by the hydrochloric acid employed practically ceased when the diameter of 0.025 mm. (0.5 mm. hydraulic value) was exceeded. It was thus apparent that the finest practicable mesh might safely be used for the "fine-earth"; and this I found to be at 0.5 mm. aperture, equal to sixty-four mm. hydraulic value. That for direct comparison by percentages it would be better to come down a much smaller grain-size, is doubtless true; but this degree of fineness would involve elaborate preparations, and difficulties that would render such investigations few and far between. I have, therefore, used the 0.5 mm. mesh in all soil analyses made since under my direction; and as the sieves used in soil work of the surveys of Kentucky and Arkansas were very nearly of the same character, that work remains comparable with mine. But whatever may be the size chosen by any one, the quantitative determination of the grain-sizes of one mm. and two mm. diameter should be made a rule, in order that allowance may be made for them when comparisons are desired.

The preliminary tests made should determine, in a measure,

¹ I omit any detailed reference to this apparatus and the subject of mechanical soil analysis for the reason that the matter has of late had considerable discussion in journals and is presented in full detail in a report to the Association of Official Chemists.

the quantities which it is desirable to use for analysis; since great inconvenience often arises from handling excessive amounts of the iron-alumina precipitate. With such balances and methods as we command at present, I do not think there exists any need of employing hundreds of grams in any ordinary cases. If in the case of ores the selling price is allowed to be governed by the assay of a few grams, it is difficult to see why in the case of a soil we should do otherwise, provided the sample has been well taken and prepared so as to be representative. If that has *not* been done, the taking of fifty grams instead of five will not help the matter much.

I usually weigh out from two and a-half to three grams for general analysis; from three to five for the (separate) determination of phosphoric acid by the molybdate method. When in a strongly clayey soil there is a great deal of calcium carbonate, so much alumina is usually dissolved as to render the handling even from the above amounts troublesome, and parting is best resorted to.

There has been a great deal of discussion in regard to the strength of the solvent to be used in soil analysis. All admit that carbonated water is too feeble to approximate to the assimilative power of plants; while "Aufschliessung" with hydrofluoric acid goes far beyond. It has appeared to me from the outset that we should, if possible, ascertain the possible maximum solvent effect that can be expected of *any* plant; and from the fact that calcium oxalate is of so frequent occurrence in roots, I have thought that oxalic acid might be regarded as the strongest solvent at their command. Now, as is well known, oxalic acid expels from the corresponding salts both hydrochloric and nitric acids. In general, therefore, it stands on a par with these; and it is from this standpoint that I originally determined to use, as the most convenient solvent, hydrochloric acid of medium strength. I have since had the question tested directly by substituting oxalic for hydrochloric acid in comparative analyses of one and the same soil; and while there were differences due to the difficultly soluble compounds formed by oxalic acid, yet the interpretation of the two analyses would, for practical purposes, have been precisely the same.

A series of experiments made by Loughridge in 1873 on one and the same soil with hydrochloric acid of different degrees of concentration showed that the maximum solvent effect was exerted, not by the strongest acid, but by that of about 1.115 sp. gr. I therefore adopted this as the standard acid for soil analysis. Another series of experiments showed that the action was made practically complete by a digestion on the steam bath for five days; this also was, therefore, adopted as the regulation time for the acid digestion, which is always done in a porcelain beaker covered with a watch glass, only half immersed in the steam so as to permit condensation of the acid volatilized. My practice has been to take ten times as many cc. of acid as grams of soil weighed out.

The analysis is then carried out essentially like that of any silicate, including the determination of the silica soluble in sodium carbonate solution, which is a very important datum in estimating the degree of decomposition and zeolite formation that has occurred in the soil. In most cases the silica so determined permits of being assigned to the alumina dissolved, as kaolinite; but to this there are numerous exceptions, there being often twice as much alumina as can be assigned to the silica set free by the acid. The only possible form in which this excess of easily soluble alumina can be present is that of *aluminum hydroxide*; which must, therefore, be considered as one of the normal constituents, notably in the case of highly calcareous, and especially of "alkali" soils.

The phosphoric acid is determined by the molybdate method in a separate and larger portion of material, which is previously ignited in order to determine the "loss by ignition." This latter item, while serving to make the result of the analysis sum up to 100 or thereabouts, is really of no practical significance; since it is made up, besides the combustible matter, of water of hydration from the kaolinite as well as from the various hydrates present, and in calcareous soils of carbon dioxide, which can not be restored by treatment with ammonium carbonate, but must, if necessary, be determined in a separate portion and properly deducted. The combustible portions of the soil farther consist of two distinct portions, namely, humus ready-formed,

and unhumified vegetable matter; so that even if we were able to segregate the water belonging to the several hydrates, we would still be unable to estimate the true humus contents. This can only be done by the method of Grandeau, *viz.*, treatment of the soil first with weak acid and then, after washing, with weak ammonia water, evaporating the filtrate and igniting the residue. The methods of wet or dry combustion usually prescribed for humus determination yield results varying widely with the season, and incapable of serving as the basis of general conclusions; since it is quite uncertain whether or not the unhumified matter will ever become humus, or will be eliminated (as is largely the case in the arid region) by *eremacausis*, or (in the humid region) by fermentation.

In the ash of the humus, at least phosphoric acid should always be determined, since the phosphoric acid thus contained is certainly more available to plants than that not dissolved in the Grandeau treatment, although not as fully so as was at first claimed by Grandeau. The bulk of the humus ash is usually silica, which should be weighed, since we thus gain an idea of the amount of other ingredients contained in the "*matiere noire*." But ordinarily I do not consider a farther prosecution of this analysis as of material practical importance.

The humus percentage gives an approximate idea of the nitrogen store in the soil, the percentage of nitrogen in the "*matiere noire*" being usually three to five per cent. While this is true for the region of summer rains (the "humid"), it seems that in the arid region the nitrogen percentage in the humus is so much greater, that a direct determination alone can serve the purpose. This is readily done by substituting in the Grandeau process a solution of potash or soda for that of ammonia, and after neutralizing the filtrate, evaporating and determining the nitrogen by the Kjeldahl method.

The direct determination of nitrates and ammonia in soils is in my view usually of little interest for general purposes, outside of the arid region, where these compounds remain wholly or partially in the soil and may accumulate to a considerable extent. In the humid region they are usually present in such minute proportions and subject to so much change from day to

day, that for the purpose of judging the soils' general resources in nitrogen such determinations are of little use. When made they should, of course, be done by leaching with water and treatment of the filtrate, since we have no method by which the determination can be made in the whole soil without attacking also the nitrogen of the humus.

The determinations mentioned are in my view all that is usually called for in the examination of soils for practical purposes; very commonly, a general knowledge of the soils of a large region may render a goodly proportion of the determinations unnecessary. Thus the soils derived from the great eruptive sheet of Oregon and Washington have proved to be so universally rich in phosphates, that even this important determination frequently becomes superfluous; and almost the same can be said for potash and lime throughout the arid region. In a large number of cases it is only necessary to identify the soil under examination by mineralogical analysis with others of the same type previously examined from the same region; and this identification naturally carries with it the conclusions previously deduced from observation in the field and laboratory, with very little trouble.

It now remains for me to consider briefly what are the conclusions and practical deductions legitimately flowing from such work as I have outlined. I have heretofore published some detailed discussions of this subject, and will therefore not go into illustrative details, for which I refer to those publications.

What practical meaning shall we attach to the percentage data found by analyses made as described above? How much of each of the important ingredients must be present in order that the soil may be considered "rich" or "poor?"

In this general form the question is unanswerable, as is shown by the comparison of even a very few soils noted for great and lasting productiveness. Manifestly, cultural experience alone can answer the question in *any* form; and it is precisely upon such experience that I have based the general rules I shall enunciate—not *ex cathedra*, but purely as the result of extensive *comparisons of the results of chemical analysis of virgin soils with cultural experience*.

(1) There is one invariable rule as regards plant-food percentages, to which in virgin soils I fail to find a single exception. It is that all having high percentages are highly productive, unless physical conditions render them uncultivable.

(2) The reverse is by no means generally true, for there are soils having what must be considered very low percentages that nevertheless prove both immediately productive and of considerable durability.

At first blush this admission seems fatal to the claims of chemical soil analysis to practical utility. It certainly proves that such analysis is not to be relied upon, *alone*, to determine the quality of a soil; it must be supplemented by other data than the plant food percentages.

When we discuss the cases forming this class of apparent contradiction, we find, first, that the soils so circumstanced are almost invariably rather coarsely sandy ones, and of considerable depth. So soon as we throw out of consideration the great mass of obviously inert material and examine the "fine earth" corresponding to the grain sizes of rich clay soils, our percentages assume quite a different magnitude, particularly when the great depth to which plant roots can exercise their vegetative functions in pervious soils are taken into consideration. Three other conditions must, however, be fulfilled in order to render such soils of low percentages thrifty; namely, the *ratios* of the several ingredients among themselves must not fall below certain values. In following up the investigation of these ratios, the substance which assumes commanding importance is *lime*. Unless lime is present in sufficient proportional amount to insure the presence of a certain proportion of calcium carbonate at all times, the soil will lack thriftiness; and this is true of all soils, whether of high or low percentages. Moreover, it is strikingly true that the percentage of lime required to fulfill this condition is decidedly higher in clay soils than in sandy ones.

The existence or absence of this important condition is in general readily recognizable by the vegetation characterizing calcareous soils; and one of the first points that must strike the observer is that "lime plants" are, almost throughout, those

upon which old farmers base their successful locations of good land. But in following up this indication we soon find that we must abandon the definition of calcareous soils usually given in text-books ("soils that effervesce with acids"); for all the advantages of calcareous soils are secured with percentages of lime far below those in which the slightest effervescence can be perceived. Here, then, soil analysis renders the essential service of enabling us to account for the choice made by experienced frontiersmen and land experts; practically, *they are in quest of calcareous lands!*

That "a limestone country is a rich country" is an old adage, easily verified by any one who observes the geological map as he travels. But the adage holds true not only of limestone districts, but also of those which from other causes have a notable proportion of lime in their soils. The most striking example of the latter class is the entire arid region, of America as well as of Asia and Africa. As I have more elaborately shown in a special treatise (A Report on the Relations of Soil to Climate; Bulletin No. 3 of the U. S. Weather Bureau), the presence of a notable amount of calcium carbonate in the soils of arid countries is the necessary result of the failure of the scanty rain-fall to leach out the water-soluble products of the weathering process; foremost among these, calcium carbonate is accumulated even where no limestone formations exist. According to the adage above quoted, then, arid countries ought to be rich countries. History shows this to be true, with the proviso that there is any soil at all; for the slowness of the weathering process in arid climates renders soil formation correspondingly slow. Arid climates, moreover, necessitate irrigation; but where, as in Egypt and India, the needful water is supplied, the soil proves almost inexhaustible. It need hardly be mentioned that alongside of lime, other important ingredients accumulate in the soils of the arid regions; notably, *potash* and *nitrate*s.

The good results of the presence of much lime in soils, about which there can be no practical question, is doubtless connected partly with the effects which must be attributed to calcium carbonate in the soil as well as in the laboratory: It acts in the "Aufschliessung" of silicates, and it is doubtless from this

cause that (as was mentioned above) we find such large amounts of soluble alumina in calcareous clay soils. Moreover, lime favors *nitrification*, and prevents the formation of injurious *acidity*. That much we can say with certainty; but it has doubtless other important functions, even in a chemical point of view; while as a flocculator of clay it performs a most important physical office, in promoting easy tillage, and circulation of water.

In very sandy soils, as little as 0.10 per cent. of lime may cause the soil to show "lime vegetation;" while in very heavy clay soils, I have known even 0.6 per cent. to be inadequate for this purpose. But apart from the most extreme cases, I find we may safely augur favorably of any soil containing *as much lime as potash*.

The average ratio of the lime percentages of soils in the arid and humid regions I find to be about twelve to one, if we exclude from comparison, on both sides, limestone soils proper. The most general expression I can give to the results of my discussion of the analyses of virgin soils with respect to lime, is that in its presence (in adequate proportions) much smaller percentages of the other plant foods will suffice for high and lasting productiveness; and that much less lime suffices to produce this effect in "light" than in "heavy" soils. It thus appears, then, that the question of the adequacy of plant food percentages is largely dependent upon the proportion of lime, as well as upon the physical character of the soil. The latter point depends essentially, of course, upon the greater facility with which an extended root-development occurs in light than in heavy soils.

I think that the failure of agricultural chemistry to recognize as fully as it deserves the extreme importance of lime in soils, is measurably due to the accidental fact that partly extended limestone formations, partly the prevalence of the mixed glacier drift over the greater part of Europe and Eastern North America, have made calcareous soils so predominant in the regions where agricultural science has been developed, that the exceptional and relatively unimportant non-calcareous areas have escaped attention.

As regards *potash*, the comparisons I have made of hundreds

of analyses from the arid and humid regions of the United States, respectively, show that potash, like lime, accumulates to a remarkable extent in the soils of the arid climates, doubtless in the form of zeolitic compounds; the average proportion in the two regions being about one to three in favor of the arid. Coupled with the fact that there, potash salts are often abundant in the soil water, as well as in the waters of the streams serving to irrigate these lands, the conclusion that potash is not likely to be soon called for as a fertilizer in that part of the continent becomes natural, and is abundantly confirmed by all tests thus far made. The invariable presence of an excess of lime in the arid soils, moreover, promises the current setting-free of potash from the soil zeolites.

The general average of potash in the arid soils is from 0.7 to 0.8 per cent.; for the humid soils of the Cotton States, from 0.21 to 0.25 per cent. No wonder that, considering the frequent deficiency in lime in the latter region, the Stassfurt salts are among the first of the effective fertilizers for the Eastern United States.

As regards *phosphoric acid*, the comparison of the soils of the humid and arid regions fails to reveal any constant difference; its presence in larger or smaller proportions being, apparently, dependent entirely upon local geological and petrographic conditions. It is curious that in my investigations of virgin soils I have been led to the identical figure for the minimum percentage of this substance that will still insure profitable culture, that, I find, has been accepted by European investigators; namely, five-hundredths of one per cent. (0.05 per cent.). When no more than this amount is found to be present in any soil, production will soon cease unless phosphatic fertilizers are used; the duration of profitable culture depending materially, however, upon the proportion of lime present. Anything much above one-tenth of one per cent. usually proves, in virgin soils, to be quite a full supply, rendering the use of phosphates ineffective for a number of years.

Owing to the difficulty formerly existing in the *nitrogen* determination in soils, my investigations in this direction have not been as extended, nor the results as conclusive, as in the case of

the mineral ingredients. Taking the humus determined according to Grandeau as an approximate gauge of the nitrogen store in soils, it would seem that in the humid region—the Cotton States in particular—less than 0.5 per cent. of humus, estimated to contain say an average of five per cent. of nitrogen, constitutes a deficiency; while in the arid region, as before noted, less than half that amount seems to suffice, rendering the use of nitrate fertilizers ineffective. But owing to the faultiness of the methods employed, the data thus far existing are, as yet, too scanty to serve profitably for the discussion of these points.

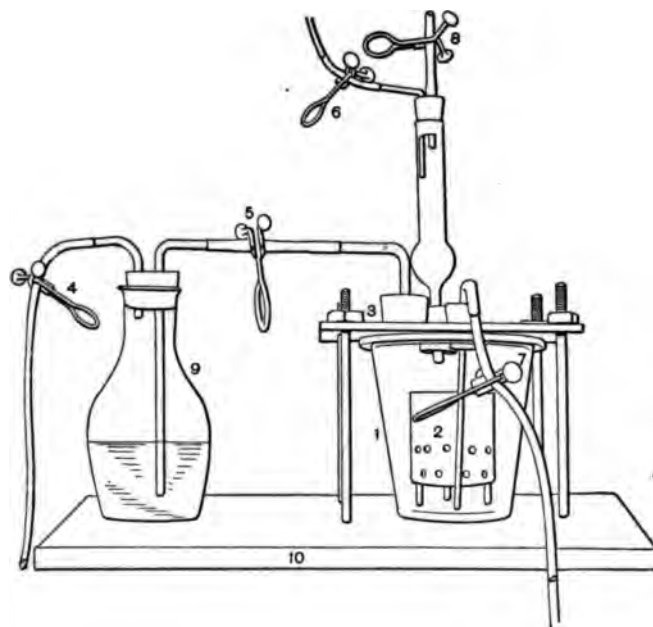
In summarizing the outcome of my studies on the relations of the actual productiveness of virgin soils to their plant food percentages, I might say that they support the intrinsically reasonable general thesis that *the amount of available plant food in virgin soils of essentially similar origin is sensibly proportional to the respective totals of such ingredients found by analysis*; provided we take into consideration both the proportions of these ingredients among themselves, and the physical nature of the soil. It is abundantly evident that sandy, pervious soils can, owing to the greater root-development they permit, be fertile with much smaller percentages than those which are difficult of penetration; at the same time, there is an obvious limit beyond which this greater root surface cannot make up for too great a scarcity of one or several ingredients. The test of how far the dilution of a close, fertile soil with pure sand can be carried without detriment to production, is apparently easy to make; and yet these experiments encounter no inconsiderable difficulties in actual execution. Yet their importance is so fundamental that I propose to prosecute them as diligently as circumstances permit, and earnestly hope that others will work in the same line of research.

HYDROGEN SULPHIDE GENERATOR.

By H. A. BISHOP.

Received Nov. 27, 1893.

THE accompanying figure represents a very useful contrivance for the generating of hydrogen sulphide. It consists of 1, an ordinary glass tumbler placed upon a wooden base 10. 2 is a leaden cylinder pierced with small holes. Between



1 and 3 is a rubber washer which makes the generator complete when 1 is held in place by four bolts as seen in the figure, 9 is a wash bottle. When iron sulphide has been placed in 2, the apparatus is ready for generating hydrogen sulphide, first by opening first cock 4, then 5, and finally 6, which allows the acid to enter 1, from a supply receptacle. When the acid has risen above the holes in 2, 6 is closed and all is in operation. After sufficient H_2S has been obtained 4 is closed first, then 5, and 7 is opened after which 8, which is connected with a water bottle which allows water to wash out what acid remains. The working and construction is very simple.

THE USE OF ELECTROLYSIS IN TECHNICAL CHEMICAL PROCESSES.¹

By J. W. LANGLEY, CLEVELAND, OHIO.

TECHNICAL chemistry covers a very wide field stretching from metallurgy on one side to the production of the most delicate colors and odors on the other, in all of which, possibly, electricity is destined to play a part although up to the present time it has only been used to any important extent in the division including the chemical side of metallurgy. Here by far the most notable examples of its use are in the purification of copper and in the extraction of aluminum.

The electrolytic separation of pure copper from crude copper is substantially only a large expansion of the old processes of electrotyping and electroplating, and therefore does not offer much which is novel, but the production of aluminum from its oxide is a typical example of an electro-metallurgical operation. I propose, therefore, to describe somewhat in detail the method employed as it will serve to indicate the steps and precautions to be observed in the applications of electrolysis to other metallic compounds.

The electrolytic production of aluminum is an industry only five years old, but in that short period it has completely revolutionized the manufacture of this metal; indeed it is to-day the only successful method and will probably remain for a long time without a competitor. In this country the process is carried on only by the Pittsburgh Reduction Company, at New Kensington, Penna., which manufactures under broad patents granted to Chas. M. Hall, the discoverer and patentee of what is now generally known as the Hall process.

The very important discovery which is the foundation of this method is the fact that oxide of aluminum is soluble in certain double fluorides in a fused condition, the salt which operates the best for this purpose must be composed of fluoride of aluminum and of a fluoride of a base more electro-positive than aluminum; sodium, potassium, and lithium fulfill this condition, but on account of expense fluoride of sodium is preferred. The

¹ Read before the World's Congress of Chemists, August 25, 1893.

mineral cryolite $\text{Al}_2\text{Na}_2\text{F}_{12}$, or as it may also be written $\text{Al}_2\text{F}_6(\text{NaF})_2$, is a native fluoride coming within the requirements of the class of double fluorides necessary and it forms the principal solvent used. Only, as its melting point is somewhat high, it is an advantage when not operating on a very large scale to add to it small amounts of other fluorides to bring down the fusing point.

Cryolite will dissolve more than twenty-five per cent. of its weight of alumina forming a clear and colorless solution from which the metal can be readily electrolyzed.

There are some features of theoretical interest about this act of solution, for that it is a solution rather than a chemical compound there can be no doubt. Alumina when added to the melted salt dissolves quietly without effervescence or any manifest evolution of heat, resembling in all respects the solution of salt or sugar in water. But alumina is not appreciably soluble in melted sodium fluoride, and aluminum fluoride by itself is infusible except at extremely high temperatures. The presence of both fluorides is absolutely essential. The two fluorides may be taken initially as a double salt or they may be separately mixed with alumina, the final result is the same, *viz.*, the perfect solution of the oxide.

The electrolytic decomposition of the dissolved oxide is carried out on a manufacturing scale by using carbon electrodes. A rectangular vessel made of iron boiler plate is lined with compressed carbon to a thickness of from four to six inches. This constitutes the negative electrode, the positive electrode is formed of carbon rods three inches in diameter by twelve in length, suspended by copper rods from a horizontal copper arm above the iron vessel. The number and disposition of these carbon anodes depends on the scale of the operation. They are hung so that they will terminate about one inch from the carbon lining, and the purpose of suspending them is that they may be easily removable one or two at a time without stopping the whole current going through the apparatus.

The iron vessel is called the pot. The melted cryolite the bath, or when it holds alumina in solution is often termed the electrolyte.

To start the operation some powdered cryolite or the mixture of double fluorides is placed on the carbon lining which is cold. The carbon anodes are then lowered till they make contact with the lining, much local heat being at once produced partly by the resistance of the carbon at the points of contact and partly by numerous short arcs formed where apposition is not perfect. This heat soon melts some of the bath material which flowing between the electrodes adds its own resistance thereby increasing the heat because there is now a larger cross section of conductor and consequently more current carried. In this way the bath material is fused and the pot finally filled. The pot may also be initially charged with melted cryolite ladled into it from a separate melting pot.

During this period while the bath mixture is fusing electrolysis is necessarily going on but it yields only a small quantity of aluminum, probably because of the access of the air and also because any fluorine potentially or actually liberated finds some of the metal in a finely divided and diffused condition with which it reunites.

When a sufficient volume of melted bath is secured the second or permanent stage of manufacture begins, powdered alumina is spread over the top of the bath and periodically stirred down into it. It dissolves almost immediately and normal electrolysis takes place. Aluminum is deposited in a melted condition at the bottom of the bath against the negative electrode, while the oxygen which is transferred to the positive side burns the anodes escaping as carbon monoxide and carbon dioxide. The anodes are thus consumed and must be from time to time pushed down further into the bath. The melted fluorides are not electrolyzed and may be used over and over again indefinitely, it being only necessary to add enough to supply the small losses principally of a mechanical nature occasioned by the removal of the metal. The operation is strictly continuous, alumina is added on the top of the bath and the metal is ladled out from the bottom.

There is quite a complicated adjustment of chemical and electrical forces concerned in the successful electrolysis of alumina which are interesting from the stand point of pure science.

The current employed by the Pittsburg Reduction Company is 7000 amperes. In order to send this through a bath of melted fluorides only, with the usual current density requires fifteen volts, but as soon as alumina is added the pressure promptly falls to from six to seven volts which is that necessary for the normal working of the process. This E. M. F. is obviously consumed in two ways: First, by the force of polarization necessary to break up a molecule of Al_2O_3 ; second, by the fall of potential due to the resistance of the anodes and of the bath. It is possible to calculate this work both in chemical and in electrical measures.

The heats of formation of one molecule each of the bath constituents is as follows:

| | |
|-------------------------|------------------|
| Sodium fluoride | 109,700 calories |
| Aluminum fluoride | 550,000 " |
| Aluminum oxide | 388,920 " |

The electromotive force of decomposition depends, as is well known, on the equivalent and not on the molecular weight and these will be $\text{Al}_2\text{O}_3 = \text{Al}_2\text{F}_6 = 6 (\text{NaF})$.

The energy of 22,900 calories is proportional to one volt, according to Sir William Thomson, therefore the E. M. F. of decomposition will be:

| | |
|-------------------------|---|
| Sodium fluoride | $\frac{109700}{22900} = 4.8$ volts |
| Aluminum fluoride | $\frac{550000}{22900 \times 6} = 4.0$ volts |
| Aluminum oxide | $\frac{388920}{22900 \times 6} = 2.8$ volts |

Thus the oxide of aluminum is the weakest body present and the only one to be decomposed provided the current density is not permitted to become too great.

The fact that no appreciable quantity of fluorine is given off, but only oxygen, when the pots are working at normal voltage and current is perfectly explained by the above theoretical values of the electromotive force of decomposition. The direct measurement of this force presents considerable difficulty on account of the variation of the resistance of the bath with its temperature, but the best estimates from actual measures show that the breaking stress of one-sixth of a molecule of alumina is certainly less than 3.5 volts. Thus the theoretical number is fairly well sustained by practical observation.

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 el solely to produce heat.

of the application of electrolysis to an
 s the refining of gold and silver, but more
 The practical details as carried out by the
 ed Company, of Pittsburg, Pa., under the
 are as follows:

Tanks are made and divided into compartments so that they may be connected up in series. The unit compartment is 18" x 24" x 17" deep, and seventy of these are in the circuit at one time. Each compartment has three anodes, 10" x 20" x $\frac{1}{4}$ ", and four cathodes of about the same area as the anodes. The anodes are composed of the metal to be refined which will average 990 fine in silver, the rest being mainly copper, lead, bismuth with a little gold. The cathodes are thin sheets of pure silver. The surface exposed in each compartment, reckoning both sides of the plates, is twenty square feet, or 1,400 feet for all the tanks. The anodes are hung in a bag to catch the insoluble material which drops from them. The electrolyte is a dilute nitric acid as free as possible from sulphuric acid or chlorine. A current of 180 amperes is used and the voltage required by each compartment is $1\frac{1}{2}$ volts. The consumption of nitric acid (36° B.) is about two pounds per day for each compartment. The amount of silver deposited is, in practice, about 470 ounces per twenty-four hours in each compartment, which is equal to 1.35 pounds avoirdupois per hour. This includes all interruptions of current for all reasons. The total amount of silver refined per day is 32,900 ounces, or practically one ton. This is eighty-four per cent. of the theoretical yield for 180 amperes working the same length of time without any interruption whatever. The product is practically silver 1000 fine.

The success of this operation depends evidently on the difference of the electromotive force of silver against nitric acid, and of copper, bismuth, and lead against nitric acid, silver being the lowest. But the difference between silver and copper is not great, and a very careful regulation of current density is necessary, which, however, can be attained, making this method one of the neatest applications of electro-metallurgy and one which replaces the tedious cupellations necessary by the older process which has come down from the middle ages.

Another application, which is wholly chemical, has recently been made to the purification of sewage near New York.

Many attempts have been made to produce caustic soda and chlorine, or bleaching compounds, from common salt by electrolysis; but thus far they have not advanced to the stage of

industrial success. One of the chief reasons for this is because no insoluble anode has been discovered, for in strong solutions platinum is dissolved and carbon is oxidized and corroded; but when the liquid is weak this trouble with the anode is considerably lessened. A report by Dr. Cyrus Edson, of the Health Office, New York City, partly reprinted by the *Electrical Engineer*, gives an account of a successful experiment recently made to disinfect the sewage of the village of Brewsters which was finding its way into the city water supply. Mr. Albert E. Wolf proposed to accomplish the purification of the sewage by treating it with electrolyzed sea water. A current of 700 amperes by five volts is delivered to the water as it flows slowly past seven electrodes. Of these, four are carbon, 12" x 12" x 1" thick, while the anodes are copper coated with platinum. The flow of the solution is so limited that the salt water is electrolyzed to the proper degree and then overflows from the tank directly into the sewer. The disinfection is practically perfect. Tests show that this electrolyzed sea water equals in strength a one per cent. solution of chloride of lime. In the matter of cost the treated sea water costs 0.01 cent a gallon, while a one per cent. solution of chloride of lime costs 1.4 cents per gallon, or the sea water costs only $\frac{1}{140}$ of the lime. Compared with the cost of corrosive sublimate, the latter is one hundred times as expensive for an equal efficiency, while carbolic acid costs from two to three hundred times as much.

Other applications which have been tried and are now on their way to commercial development are: Bleaching fabrics without chlorine by means of electrolyzed acidulated water only, and the tanning of hides.

Seeing that in electrolysis we have a powerful analytic force at work heaping up products of decomposition at each pole, it would be natural to look for some means to utilize the powerful oxidizing and reducing actions of which the electrodes are the foci. This would be to save and turn to useful account the secondary reactions of the cell. A careful study of the conditions under which these secondary actions are a maximum and a minimum can scarcely fail to lead to many applications of the current in technical chemical work where electricity will be

used primarily as an oxidizing or a reducing agent and only secondarily as an agent for electrolytic decompositions.

There is one great desideratum, and that is a cheap insoluble anode. Platinum is too expensive, and carbon will not long withstand oxidation. It is this lack which to-day, among other conditions, prevents electricity from being a rival to the ammonia process of making soda and to the Leblanc process for producing bleaching powder as a by-product, and to its utilization as an oxidizing agent. When the cheap insoluble anode is found it will open a wide door to the applications of electricity to the chemical arts.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 1.]

THE IODINE FIGURE OF ROSIN.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received December 9, 1893.

IN the analyses of oils, and especially drying oils, one of the most useful tests is a determination of the Hübl number. The iodine figure of rosin, which is a common adulterant of oils, is stated by Benedikt (*Analyse der Fette und Wachsorten*, 171) to be 115.7; Williams (*Chem. News*, 58, 224) gives 115.31 and 114.80 for refined rosin and 112.01 and 113.28 for ordinary. Mills (*Destructive Distillation*, 13) has determined the bromine absorption to be 112.7 per cent., which would correspond to an iodine absorption of about 179. In order to throw some light on the causes of this disagreement, experiments were made to ascertain the effect of different amounts of iodine in excess, different times of absorption and different qualities of rosin.

Five samples were used representing different grades from "W.W." (water-white) rosin to "A" (black).

In the tests made to ascertain the influence of time and of excess of iodine the rosin used was that known as W.W., which is the best grade in the market. The iodine solution used contained twenty-five grams of iodine and thirty grams of mercuric chloride per liter, and the thiosulphate solution 24.8

grams of sodium thiosulphate per liter. The thiosulphate solution was standardized by means of a solution of potassium dichromate made from chemically pure dichromate which had been further purified by several recrystallizations. The tests were made in bottles of 250 cc. capacity, having carefully ground stoppers, such as are used in the assay of silver bullion. The rosin was in each case dissolved in ten cc. of chloroform and the absorption was effected in a dark closet.

The results were as follows:

| Quality of rosin. | Quantity, grams. | Excess of iodine in cc. $\frac{N}{10}$ thio-sulphate. | Time of absorption. | Iodine figure. |
|-----------------------------|------------------|---|---------------------|----------------|
| Water-white | 0.3030 | 17.4 | 2 hours. | 142.9 |
| " " | 0.3017 | 25.4 | 2 " | 146.4 |
| " " | 0.3048 | 33.2 | 2 " | 148.5 |
| " " | 0.3010 | 50.2 | 2 " | 152.1 |
| Water-white | 0.3007 | 13.35 | 1 hour. | 126.7 |
| " " | 0.3027 | 11.6 | 2 hours. | 133.1 |
| " " | 0.3003 | 10.5 | 4 " | 142.0 |
| " " | 0.3023 | 8.8 | 8 " | 144.8 |
| " " | 0.3087 | 11.55 | 18 " | 160.3 |
| " " | 0.3033 | 1.9 | 52 " | 172.6 |
| "A" (black) | 0.3055 | 20.25 | 18 hours. | 143.6 |
| "E" | 0.3012 | 14.2 | 18 " | 156.4 |
| "G" | 0.3054 | 13.7 | 18 " | 153.1 |
| "W.G." (window-glass) | 0.3160 | 9.7 | 18 " | 164.2 |
| "W.W." (water-white) | 0.3087 | 11.55 | 18 " | 160.3 |

It appears from these results that the average iodine absorption in eighteen hours by different qualities of rosin is 155.5, the average quantity of rosin used being 0.3073 grams and the average excess of iodine equivalent to 13.88 cc. $\frac{N}{10}$ thiosulphate. The darker samples of rosin absorb less iodine than the lighter ones which have been subjected to less heat. The variations due to different lengths of time and different amounts of iodine in excess are, however, so serious that comparatively little can be learned by Hübl's process as to the nature of an oil when rosin is present in any considerable quantity.

AN IMPROVED FILTER-DISK.¹

BY MAX KAEHLER.

AN obstacle to the extended use of the porcelain filter-disks, introduced by Otto N. Witt, (*Ber. d. chem. Ges.*, 1886, 918), has existed in the great difficulty of securing a uniformly tight joint between disk and funnel. On the one hand it was necessary to have funnels whose walls were not only perfectly smooth, but were inclined at an angle of exactly 60° . On the other hand any irregularity on the side of the disk seriously affected the tightness of the joint, and frequently, even when the oblique position was scarcely evident to the eye, caused the cracking of the funnel.

These difficulties have been overcome by the introduction of a

modified form shown in the accompanying sketch. The disks are made with a rather deep groove running around the side, in which is held a stout rubber ring (c), projecting a slight distance beyond the adjoining surface. The disk is further perforated in the center by a funnel shaped opening, into which is adjusted a glass rod (a) which extends down into the neck of the funnel. The rubber ring produces a perfect joint while the glass rod keeps the disk in a horizontal position. When large disks and wide necked



funnels are used a cork with channeled sides and fitting closely in the funnel's neck is slipped over the lower end of the glass rod.

¹ Read before the Cincinnati Section, December 15, 1893.

The new device assures rapidity and certainty in manipulation with complete absence of danger to the funnels employed.

These new disks are manufactured by Kaehler and Martini, of Berlin, Germany.

QUANTITATIVE WORK FOR BEGINNERS IN CHEMISTRY.¹

By W. A. NOYES.

IN most of our chemical laboratories the work which is given to beginners is chiefly or altogether of a qualitative nature. In many schools and colleges the work begins with a study of the qualitative properties of a series of chemical elements and their compounds, chiefly of gases and metalloids. In other schools the students begin at once with the study of qualitative analysis. A large majority of our students never get beyond this first stage and it is safe to say that they acquire but a very slight knowledge of real chemical work. The work which is done in our scientific and technical laboratories and in chemical factories consists almost entirely of quantitative analyses or of the preparation of chemical substances carried out in an accurate quantitative manner. Indeed, we are accustomed to say that the science of chemistry began with the use of the balance and we all recognize the extreme importance of quantitative relations in most of our chemical work.

We must keep in view several objects in selecting the laboratory work for beginners. First they should become personally acquainted with the appearance and properties of a number of the chemical elements and their compounds. The acquisition of a large amount of knowledge of this kind is desirable but we may easily make the mistake of endeavoring to impart too much. A few topics exhaustively studied will prove of greater value than a superficial study of a great many. This is especially true of qualitative tests with solutions. A beginner can apply a great many such tests in a comparatively short time, but unless his powers of discrimination and of memory are very unusual he will retain only a confused recollection of his work. A second object is to secure a training in delicate and accurate manipulation and in the use of different forms of apparatus. A third

¹ Read before the World's Congress of Chemists, August 26, 1893.

object is to fix in the mind of the student knowledge which may have been imperfectly acquired by watching the demonstrations of a lecturer or by the study of a text-book. Some teachers carry this thought so far that they seem to imply that no knowledge of a topic can be really acquired by the student until he has demonstrated it by personal experiment. Indeed I have heard some teachers contend that they would not allow a text-book in the laboratory, but would have their students acquire all of their knowledge at first hand by their own experiments. Such a principle if logically carried out could never take the student beyond the stage of alchemy, for the student of to-day is no better able to develop a science of chemistry for himself than was the old alchemist. And if you direct his experiments in such a way as to develop and elucidate the science as it is now known, you have forsaken the principle just as much as though a text-book were used.

It seems to me that such views arise from a mistaken conception of the real nature and purpose of laboratory instruction. After all, the method of personal experiment is a very slow and laborious method of acquiring knowledge. Only a very small fraction of our knowledge of a science, if that knowledge is by any means adequate, has been acquired in that way. It is true that the method is absolutely essential for beginners, and I do not think that any of us get beyond the need of it. The man who never uses a balance or handles a test tube will not for very long be a strong factor in the advancement of chemical science. But the method of laboratory instruction is essential, not because knowledge can not be acquired in other ways, but because at the start the imagination of the student is deficient and it is only by means of personal experiments of his own that he can acquire the ability to understand and appreciate the experimental work of others. The memory is also deficient and the personal work on a subject may be of great value for that reason, as well. But the things which we should endeavor to secure in laboratory instruction are, first, such an acquaintance with experimental methods as shall enable the student to thoroughly grasp the solid experimental basis of the science and give him the mental habit of referring everything back to the rigid ex-

perimental test; and second, the ability to do accurate and independent experimental work himself. No student can demonstrate for himself more than an infinitesimal number of experimental facts in comparison with the vast array of such material which has been accumulated.

If the principles which I have suggested are correct we should endeavor to secure as thorough a knowledge as possible of experimental methods, and neatness and accuracy in laboratory technique rather than the illustration of as large a number of details as possible. These results can be secured more fully by a series of quantitative problems than by a large amount of merely qualitative work. I do not mean by this that qualitative work is not necessary and desirable as well, but for the beginners, especially, quantitative work is of more value. In order to make my meaning more clear I will give a few illustrations. One of the earliest problems that I give is the determination of the weight of a liter of hydrogen essentially by Regnault's method. A bulb containing about one-half a liter and bearing a three way cock is exhausted with a Bunsen pump and the residual pressure determined with a manometer. The bulb is then weighed, using a sealed counterpoise of nearly the same volume, then filled with hydrogen, temperature and pressure noted, and weighed again. The results obtained by careful work are usually one or two per cent. too high. A similar determination of the weight of oxygen gives results with a far smaller percentage error. The determination of the amount of oxygen in potassium chlorate by heating about a gram of the salt in a small porcelain crucible placed within a second gives a good illustration of the law of constant proportion. The preparation of potassium perchlorate can be made to furnish a considerable amount of valuable instruction. The capacity of a bottle holding about two liters is determined, a calculation of the amount of potassium chlorate required to give oxygen enough to fill it when only the first stage of the reaction is used, is made and the experiment performed. Then the potassium chlorate and potassium perchlorate are separated and the latter is purified by crystallization. A study of the qualitative reactions which distinguish potassium chloride, potassium chlorate and potassium perchlorate

is made and the tests to establish the purity of the last are applied. Finally a determination of the amount of oxygen in potassium perchlorate gives, in connection with the last problem, an illustration of the law of multiple proportion. I will give but one further illustration—the determination of the relative atomic weights of hydrogen, chlorine, and silver. A known weight of pure silver is dissolved in nitric acid, precipitated with hydrochloric acid and the silver chloride weighed on a Gooch crucible. In a dilute hydrochloric acid the amount of hydrogen is determined by allowing ten cc. of it to act on an excess of zinc in an appropriate apparatus, the hydrogen being measured in a gas burette, accurate corrections being made for temperature, pressure, and aqueous pressure. In another known volume of the same acid the chlorine is determined by precipitation with silver nitrate.

By a careful selection of problems it is possible to give the student, within a reasonable time, practice in the careful use of the more common forms of chemical apparatus. In other words the student can make a beginning at working as a chemist works instead of doing scarcely more than play with bottles and test tubes. Among other advantages of this method of instruction is the fact that the results which are obtained are usually a fairly good criterion by which to judge of the care with which the student has worked, and the student soon finds that careless work will not give good quantitative results. Also the student dwells long enough on a problem so that many details become thoroughly fixed—a result that is rarely obtained in qualitative work, except by means of many repetitions. I am aware that there are some practical difficulties in the way of carrying out the methods which I propose, especially in the matter of apparatus, but these difficulties are not nearly so great as they appear at first sight and I am sure that they are not greater than those which have been overcome in many of our physical laboratories.

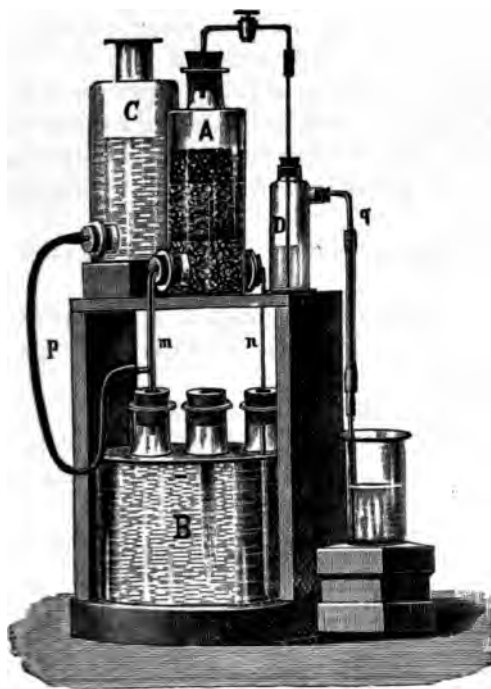
A NEW HYDROGEN SULPHIDE GENERATOR SPECIALLY ADAPTED FOR USE IN ANALYTICAL LABORATORIES.¹

BY L. L. DE KONINCK.

THIS new form of generator has yielded such excellent results, especially in connection with quantitative work, where the need of a constant, easily regulated current of hydrogen sulphide is so often felt, that a detailed description of its construction and handling is now made public.

The arrangement of the different parts is shown in the accompanying cut, in which A, the generator proper, rests upon a

wooden support. It consists of a large wide-necked bottle, provided at the lower part with two tubulures, opposite one another. The bottom is covered with a thick layer of broken glass or porcelain. A three-necked Woulff's bottle, B, of ample size, but low form, is placed beneath the wooden support. The tube n passes from A to the bottom of B. The tube m passes likewise from A to B, but terminates immediately beneath the stopper, while its branch is connected



by means of rubber tubing p, with the tubulure of the movable pressure bottle C. The outlet tube of A, provided with a glass

¹ Read before the Cincinnati Section, November 15, 1893.

cock, enters the wash flask D, from whence gas can be directed at will through q. The middle neck of B can be used for the introduction of a syphon in charging or emptying the apparatus.

The method of using the apparatus is exceedingly simple. A receives a full charge of iron sulphide. B and C are filled with acid, and the latter placed upon a block at the proper elevation. When the cock above A is opened the acid flows into A, the generation of hydrogen sulphide begins, and the gas streams out through the wash bottle D. As ferrous chloride forms in A, its solution on account of its greater specific gravity, sinks continually downward through n, to the bottom of B, while fresh acid enters to take its place. A circulation is thereby established first of strong acid and then of acid containing gradually increasing amounts of ferrous chloride, until the point is reached where nearly the entire stock of acid is changed into ferrous solution. The rapidity of the liberation of the gas can be controlled by raising or lowering C, as well as by the adjustment of the cock in the outlet tube. The current is stopped by lowering C and placing it along side of B, but so that its neck is higher than those of B.

From the above the following advantages of this new apparatus will be easily understood:

1. The current of gas is uniform throughout a given operation, standing under a pressure of 20-30 cm. of water, and capable of being regulated at will.
2. When not in use the pressure is removed and there is no possibility of wasting material either by accident or otherwise.
3. A practically complete utilization of the acid employed is attained.
4. The parts of the apparatus are simple and easy to replace in case of breakage.

It is, of course, evident that the apparatus can be charged with marble or zinc and used to generate carbon dioxide or hydrogen under the same advantageous conditions.

The complete apparatus is constructed in a satisfactory manner by the well-known instrument manufacturers, Max Kaehler and Martini, of Berlin.

LABORATORY NOTES.

BY JAMES S. DEBENNEVILLE.

Received December 7, 1893.

BERYL.

In determining the alkalies in a beryl from Fahlun, Sweden, the percentage of potash seemed worth noting. In the analyses of beryl accessible to me I find potash put down as one of the constituent alkalies but undetermined. (J. S. Diller Hillebrands Min. Notes, Bull. 55 U. S. Geol. Survey in the case of a white beryl from Winslow, Me.) F. C. Robinson (*J. Anal. Appl. Chem.*, 6, 510) in a beryl from near Yarmouth, Mass., also notes the presence of phosphoric acid. Beryl from the localities noted in *Dana's Mineralogy*, sixth edition, do not give this alkali. In making the examination the platinic chlorides of cesium (when present) and potassium were boiled with small portions of water until the cesium lines appeared sharply in the spectroscope. The potassium salt was subsequently examined for cesium, with negative results. Other specimens of beryl were then examined and all were found to contain notable quantities of potash. The only contamination appeared to be a little ferric oxide. Nos. I, II, and III, were given to me by the late Dr. F. A. Genth to whose kindness I owe not only the specimens but the constant advice and supervision he gave so freely to those studying under him. No. IV was obtained from Geo. L. English and Co., of New York.

Analyses gave:

- I. Fahlun, Sweden, dull yellow. In small grains. Sp. gr. 2.713.
- II. Black Mt., Buncombe Co., N. C., apple green. Vitreous. Manganese trace. Sp. gr. 2.748.
- III. Acworth, N. H., light green. Vitreous. Sp. gr. 2.714.
- IV. Acworth, N. H., light green. Vitreous. Sp. gr. 2.730.

| | I. | II. | III. | IV. |
|--------------------------------------|-------|-------|-------|-------|
| SiO ₂ | 64.02 | 66.24 | 65.23 | 66.53 |
| Al ₂ O ₃ | 16.44 | 17.64 | 17.72 | 17.11 |
| Fe ₂ O ₃ | 0.68 | 1.36 | 1.35 | 0.94 |
| BeO | 12.91 | 11.06 | 12.37 | 12.24 |

LABORATORY NOTES.

| | I. | II. | III. | IV. |
|-------------------------------------|-------------|--------------|--------------|--------------|
| MgO | 0.23 | 0.09 | 0.37 | 0.20 |
| CaO | 0.50 | 0.36 | 0.61 | 0.43 |
| K ₂ O | 2.76 | 0.30 | 0.35 | 0.22 |
| Cs ₂ O | | | | 0.12 |
| Na ₂ O | 0.25 | 0.60 | 0.53 | 0.97 |
| Li ₂ O | 0.05 | 0.14 | 0.06 | 0.17 |
| H ₂ O | 1.76 | 2.06 | 1.49 | 1.49 |
| P ₂ O ₅ | 0.26 | 0.78 | 0.14 | trace |
| | <hr/> 99.86 | <hr/> 100.63 | <hr/> 100.22 | <hr/> 100.45 |

COPPER ANALYSIS.

Experiencing considerable trouble in analyzing, for the minor constituents, pig copper and copper alloys high in copper content, a method was sought by which the great mass of the predominant constituent would remain in solution and the elements present only in small quantities would be concentrated in a precipitate of comparatively small bulk and corresponding ease in handling, the use of separate portions of the same sample for the determinations being avoided as far as possible. The method given below is based on a number of experiments conducted with the view of ascertaining the solubilities of the salts involved, under the conditions in which they would occur in analysis of a pig copper and alloy and in analyses of copper containing known quantities of the elements usually found in commercial products.

Ammonia alone being uncertain both in completeness of precipitation and from the tendency of the precipitate to run through the filter, the following modification was adopted for systematic examination of such alloys and was found to remedy the drawbacks above mentioned:

Ten grams of copper were dissolved in nitric acid. Any great excess of acid removed by evaporation. Ammonia added to resolution of the copper salt. Barium hydroxide added in excess of the quantity sufficient to precipitate the minor constituents sought. Excess is quickly indicated by the separation of a scum of barium carbonate. Filtration was made in about half an hour. The precipitate separates out rapidly. Wash well with dilute ammonia to remove any adhering copper salt. With ten grams

of copper and a dilution of 150 cc. but little copper ammonium salts separate out. Fifty grams of copper and a dilution of 500 cc. gave on standing a considerable quantity of the salts. They are, however, readily soluble in dilute ammonia on warming, the precipitate not being appreciably so. On account of the dilution the method is only qualitative for arsenic and phosphorus. For lead, bismuth, tin, iron, manganese, and antimony it is complete. Silver, zinc, and cadmium were removed from the filtrate by decolorizing with solid potassium cyanide and precipitating by hydrogen sulphide. The barium salt gives no trouble. The sulphates of lead and barium can be weighed together. The lead sulphate separated by any of the known solvents, and determined directly or by weighing the residual barium sulphate. The treatment of the precipitate containing lead, bismuth, etc., is a matter of choice.

PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

Ore Separators, etc.—511,512, December 26, Crosby, G. G., magnetic ore separator. 511,162, December 19, Roberts, F. C., puddling furnace. 510,251, December 5, Giroux, J. L., reverberatory, smelting, and refining furnace. 511,476, December 26, Vattier, C., roasting furnace. 511,090, December 19, Mathewson, E. P., furnace tap. 510,223, December 5, Wohlschlegel, C., pottery kiln. 509,890, December 5, Gonder, P., brick kiln. 510,448, December 12, Smith, M. V., coke oven. 510,051, December 5, Seymour, C. E., system of concentrating ores. 510,395, December 12, Ashcroft, E. A., apparatus for generating steam by aid of molten slag. 509,912, December 5, Jory, J. H., amalgamating sluice. 511,334, December 26, Hewett, G. C., manufacture of coke by heating coal at low temperature under pressure, consolidating into lumps, and coking in an ordinary furnace.

Iron and Steel.—511,648, December 26, Parkinson, W., converting cast-steel into wrought iron, by mixing charcoal and rolling mill scrap, reducing to spongy mass and mixing with particles of low steel and puddling. 509,973, December 5, Urick, W. P. B., method of casting solid ingots of steel. A rod is thrust into mold, then withdrawn and more molten metal is added to fill the mold. 510,340, December 5, Hines, J. H., coating iron with magnetic oxide, covering first with metal or alloy which will volatilize at a temperature below the fusing point of the iron, and then heating.

Lead.—510,979, December 19, Lunge, G., basic lead salts and caustic

alkali. Crude pig lead is oxidized and treated with nitric acid, the silver is precipitated with finely divided lead, and basic lead salts are formed by adding an alkaline carbonate and some free base. The alkaline nitrate is decomposed by ferric oxide, heated air, and steam, and the resulting ferrite is decomposed into ferric oxide and caustic alkali and nitric acid is recovered.

Copper.—510,340, December 5, Hines, J. H., ornamenting metal, after cleaning, by depositing copper, or aluminum and enameling.

Acids and Alkalies.—510,900, December 19, Cutten, E. B., electrolytic apparatus for soda and chlorine. 511,330, December 26, Fahrigh, E., process of and apparatus for obtaining ozone from the air, by absorbing oxygen, releasing the gas from the absorbent, heating, drying, cooling, and passing the electric current. 509,957, December 5, Siepermann, W., manufacture of cyanides; alkaline carbonates are subjected to a dark red heat in presence of ammonia, and potassium cyanide is separated from its aqueous solution by increasing the per cent. of potassium carbonate or caustic potash in solution.

Sanitary Chemistry.—510,825, December 12, Stratton, J. L., and Murdock, F., disinfecting apparatus. 510,756, December 12, Adam E., and Rehfuß, M. O., filter, and 510,757, same parties, sterilizing apparatus.

Brewing and Distilling.—510,827, December 12, Wiesebrock, F. W. A., manufacture of beer. 510,219, December 5, Warren, M., method of and apparatus for beer manufacture. 511,353, December 26, Mosler, J., caramel, from distilling refuse.

Bleaching and Dyeing.—511,532, December 26, Kothe, R., *et al.*, blue tetrazo dye. 511,653, December 26, Schultz, G., blue basic dye from alkalinized paradiamins. 509,929, December 5, Moeller M., blue azo dye. 511,688, December 26, Diehl, T., and Moeller, M., blue black tetrazo dye.

Tanning.—511,411, December 26, Dennis, M., tanning liquor, normal chromium chloride is rendered basic by adding a solution of an alkali or alkaline carbonate. 511,007, December 19, Zahn, W., tawing hides or skins, a composition of chrome alum and a sulphide of an alkali is used. 511,301, December 19, Lawley, W. F., method for tanning hides.

Organic Compounds.—511,303, December 19, Majert, W., piperazine, $C_4H_{10}N_2$, anhydrous, with caustic properties, a solvent of uric acid. 511,708, December 26, Moeller, M., amido-naphthol disulphonic acid. 511,450, December 26, Noyes, A. A., and Clement, A. A., paramidophenol-sulphonic acid, made by electrolyzing a sulphuric acid (conc.) solution of nitro-benzol. 510,617, December 12, Stevens, J. H., and Axtell, F. C., compound of pyroxylin, containing pyroxylin, phenyl acetamide, acetone, and a liquid menstruum. 510,132, December 5, Hagemann, O. C., separating tannin, dissolving tannin from substances containing it in amyl alcohol and separating the alcohol. 511,143, December 19, Higgin, W. H., manufacture of sodium acetate from "esparto liquors," by evaporating water, and treating residue carefully above 200° C., but not high enough to decompose the sodium acetate.

Oils and Varnishes.—510,050, December 5, Scollay, G. W., siccatives, formed by adding to a vegetable oil a metallic oxide. 510,734, December 12, Trageser, A. F., apparatus for distilling and concentrating glycerol and heavy oils. 510,672, December 12, Brown, E. G., *et. al.*, "sweet residual petroleum products," purified by passing steam through petroleum while it is boiling for distillation and finally air. 511,051, December 19, Lahusen, J. C., production of neutral wool-grease.

Plaster and Cement.—509,924, December 5, Lorenz, J., artificial stone, from "ashes, cinder, burnt sand and cement." 511,735, December 26, Jones, J. K., wall plaster, sugar, 100 parts, flour, 25 parts, air-slaked slime, 250 parts, plaster of Paris, sand, and water. 510,874, December 12, Dutrey, J., artificial emery stones, sulphur, Portland cement, emery, Venetian red, and sugar form the composition. 511,740, December 26, McIlvried, J. R., retarders for plaster, air-slaked lime is kept in an air-tight receptacle and mixed with water, flour, liquid glue, and wood ashes and dried.

Miscellaneous.—510,421-22-23-24, December 12, Haley, A. E., parchmentized paper board. 509,951, December 5, Schroöder, E., manufacture of metal foil. 510,276, December 5, Lyte, F. M., electrolysis of fused metallic chlorides in a specially devised chamber. 510,834, December 12, Blackmore, H. S., electrolytic process for dissociating soluble salts. 510,065, December 5, Frédureau, J. B. F., composition of matter for crockery ware, consisting of aluminum silicate combined with a soluble alkaline salt and impregnated with fatty or resinous substances. 509,887, December 5, Fischer, J. F., and Peters, O., artificial stone filter, made by heating pulverized silica and glass to a high temperature. 510,376, December 5, Bertrand, P. H., depositing metal upon metal by immersing in solution of soluble salts of metals in dilute sulpho-carbolic acid. 510,013, December 5, Endruweit, C., method of producing metal film and metal paper. 511,271, December 19, Hoskins, Wm., safety paper for checks, made by adding to paper a soluble ferrocyanide and a per-salt of iron, insoluble in water but decomposed by weak acids in presence of a soluble ferrocyanide, and a salt of manganese, decomposed by alkalies or bleaching agents.

NEW BOOKS.

DIE SCHMIERMITTEL. METHODEN ZU IHRRR UNTERSUCHUNG UND WERTH-BESTIMMUNG. Von Josef Grossmann pp. 186. Wiesbaden, 1894. Price M. 4.80.

This treatise is a valuable addition to the literature of lubrication—and while no new methods are described, the bringing together of the various tests, as made use of by the German chemists, simplifies the subject and renders the book one of ready reference.

Especial attention is given to the subject of viscosity—both theoretical and practical—including the “internal resistance” of fluid lubricants. This latter subject has received but little attention in this country, and it is questionable if it is of much practical importance. Eight different viscosimeters are described, not one of which can be considered standard, showing that the same lack of uniformity in determining viscosity exists there as here.

The flash and burning tests are made in a manner similar to methods in use in our railroad laboratories, but the cold test is radically different and liable to error.

Evidently the very complete articles on this subject, by C. B. Dudley and F. N. Pease,¹ have not been consulted by the author. The tests, as formulated by Dudley and Pease, leave little to be desired in the way of accuracy and rapidity in the determination of the value of lubricants used in railroad practice.

The method for estimating rosin oil in mineral oil (Valenta's) could be supplemented by the process described by E. Twitchell (*J. Anal. Appl. Chem.*, 5, 379). A large portion of the treatise is devoted to descriptions of various lubricants for different kinds of machinery.

The author with many years practical experience as chief engineer of the Austrian Northwestern Railroad, gives the results of experiments in this direction, and the reasons for selecting either simple mineral oil or mixed mineral and seed-oil, for special purposes.

This portion of the work will be of value to the manufacturer of compounded oils. The treatise, while in the nature of Engineering Chemistry, is not complete enough in the qualitative reactions of the different oils and fatty acids derived therefrom to enable a chemist to accurately determine seed-oils and animal oils in the presence of each other.

If, however, Dr. Carl Schaedler's work, upon the reactions of fats and oils, be used in connection therewith, the chemist will be amply provided with the reference matter necessary on this subject.

T. B. S.

¹ *The Railroad and Engineering Journal*, 6, 76.

NOTES.

Mineral Residues in Sprayed Fruit.—Dr. R. C. Kedzie, of the Michigan Experiment Station, has examined fruit sprayed with two insecticide mixtures containing copper and arsenic. Strawberries sprayed excessively June 18 and 23 and picked June 24 contained, per pound of fruit, arsenic 0.044 grains, and copper 4.87 grains. Gooseberries sprayed June 18 and 29, July 8 and 22, picked August 2, were washed with hydrochloric acid (ten per cent.) and the washed fruit contained per pound 0.0047 grains arsenic and 0.138 copper. “In these experiments extending through two years, the minerals used in spraying the fruits were found in appreciable quantities in every instance though the amount was small in all cases except where the spraying had been purposely excessive. * * * The use of poisons in horticulture in my opinion is largely in excess of the amount required for a fungicide. One-half or even one-third of the amount usually employed would probably give as good results. * * It is safe to refuse all fruits which have been sprayed with these poisons (especially arsenic) during the period of ripening.”

It was found that a small part of the poison sprayed upon the surface of the fruit was absorbed into its substance.—*Bulletin, 101, Michigan Agricultural Exp't. Station, 19.*

Estimation of Chlorine in Water.—When the standard silver nitrate solution is employed, with potassium chromate as an indicator, it is often very difficult to decide just when the red color begins to appear, even with the comparison dish of water tinted with the chromate at hand as an aid to the eye. One sufficient reason therefor is that it is hard to compare a clear yellow liquid with one turbid from precipitation of silver chloride.

Following a suggestion of my assistant, Mr. V. H. Gridley, it is now my practice to roughly determine the chlorine present, and then to make a second determination using for comparison 100 cc. of distilled water to which has been added not only the chromate indicator, but also an appropriate amount of standard sodium chloride solution and an amount of silver nitrate solu-

tion just short of that necessary to satisfy the chlorine present. Of course if the chlorine ran so high as to render concentration unnecessary, then 100 cc. of the water itself with the indicator and the partial dose of silver nitrate would be the proper contents for the comparison dish. By these means the eye is greatly aided in noting the slightest appearance of red tint, for in respect of turbidity both dishes are alike. The results are very satisfactory.—*W. P. Mason, Rensselaer Polytechnic Institute, January 20, 1894.*

The Phenolsulphonic Acid Process for Nitrates in Water.—The interference of chlorides with this process, resulting in readings decidedly lower than the truth, is well known, but the method of determination is so easy and convenient, that it occurred to me to try the addition of sodium chloride to the comparison standards rather than abandon the process.

The "chlorine" in the water under examination having been previously determined, an appropriate volume of standardized sodium chloride solution is added to each evaporation of standard potassium nitrate solution. Thus the water to be examined, and the nitrate solutions with which it is compared, all contain the same quantity of chlorine. The results are very satisfactory.—*W. P. Mason, Rensselaer Polytechnic Institute, Jan. 18, 1894.*

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE BALTIMORE MEETING.

THE Baltimore meeting of the society held December 27 and 28, 1893, was in every respect most successful. This is due in large part to the local committee of arrangements, which in turn expresses itself as under great obligations to Prof. Ira Remsen.

The sessions were held Wednesday, December 27 and 28, 1893, in Prof. Remsen's lecture room in Hopkins Hall, Johns Hopkins University.

Addresses of welcome were made by D. C. Gilman president of the university, and Ira Remsen Prof. of chemistry.

President Gilman, in behalf of the Johns Hopkins University, extended a hearty welcome to the society and offered it all the facilities for its work which the libraries, halls, and laboratories of the university would afford. He referred to a medieval custom, the migration of students from one seat of learning to another, and compared it with the modern and American usage, which transports professors, instead of students, from one point to another. Thus the Christmas and Easter holidays, as well as the long vacation of summer, are now the favorite times for the assembling of literary and scientific associations like that now welcomed to Baltimore.

He then briefly described the buildings of the university, and made an allusion to the many distinguished men of science, from Europe as well as from this country, whose voices have been heard within the walls of Hopkins Hall where this American Chemical Society now holds its annual meeting.

Prof. Remsen in welcoming the society to the chemical lab-

oratory gave a brief account of the way the present building gradually came into being. The laboratory is called Dalton Hall, a name that has a deeper significance than appears at first sight. Dalton was a member of the Society of Friends, and the founder of the Johns Hopkins University and several of those whom he selected to act as trustees of the university were also members of this society. Certainly to every thinking chemist the name of Dalton is a most inspiring one. He gave us some of the greatest thoughts of our science, and laid the foundations of the most profitable speculations in regard to the constitution of matter. His work has been of inestimable value, and has contributed very largely to the advancement of the science of chemistry. The speaker then said that in emphasizing the science of chemistry, as he is very apt to do, he did not wish to be misunderstood. Everyone recognizes the importance of the chemical industries. These need no spokesman. The fact that pure science is not, a mere luxury, but of importance to mankind, is, however, often lost sight of, and it seems desirable that occasionally a voice should be raised in its defence. While this was not necessary on the present occasion, the speaker wished to declare his own attitude, in order, as far as possible, to avoid misunderstanding. Science and industry must go hand in hand. They are mutually dependent. The man of science who speaks with disrespect of the industries is certainly short sighted; and the same is true of the industrial chemist who speaks disrespectfully of science.

In replying to the addresses of welcome the president, Harvey W. Wiley, said that the present membership of the society was 681, of whom 542 had paid all dues. The names added during the year numbered nearly 400. He referred to the valuable work accomplished by the older members and the sacrifices they had made in order that the society might become truly, as well as in name, a national organization. These remarks applied especially to the members of what is now the New York Local Section.

There are now over 4000 professional chemists in the United States, and this allows ample opportunity for enlargement of the membership which is rapidly going on.

We rejoice that there is no longer reason that Americans should go abroad to study chemistry. Facilities equal to those offered abroad are now to be had at the Johns Hopkins University and at other institutions in our own land.

The president then read the annual address which has already been printed in the January issue of this JOURNAL.

G. F. Barker read a memorial of the late Dr. F. Sterry Hunt, at the conclusion of which the members rose to honor his memory.

After a recess of five minutes, Edward Hart was elected secretary pro tempore. The reports of the secretary, treasurer, librarian and editor were then read and adopted.

The treasurer's report follows:

TREASURER'S REPORT.

RECEIPTS.

| | |
|--|-----------|
| Balance on hand, January 1st, 1893 | \$ 518.41 |
| Cash received from dues for 1893 | 1,994.79 |
| " " " " 1894 | 200.00 |
| " " " " 1895 | 5.00 |
| " " " arrears of dues | 105.15 |
| " " " subscriptions to JOURNAL | 72.00 |
| " " " advertisements in JOURNAL | 213.45 |
| " " " sales of back numbers | 67.47 |
| " " " Initiation fee (F. J. Wulling) | 5.00 |
| " " " exchange | .07 |
| | <hr/> |
| | 3,181.34 |

EXPENDITURES.

| | |
|---|-----------|
| General expenses | \$ 380.42 |
| Journal of 1892 | 654.73 |
| " " 1893 | 1,784.70 |
| New York Local Section | 115.00 |
| Cincinnati Local Section | 59.93 |
| Providence " " | 18.33 |
| Baltimore meeting | 84.18 |
| Overpayment of Dues returned | 5.00 |
| Initiation fee returned (F. J. Wulling) | 5.00 |
| Balance on hand in bank of the Metropolis | 74.05 |
| Checks on hand | <hr/> |
| | 3,181.34 |

CHAS. F. MCKENNA, Treasurer.

No bills or claims, presented up to date and audited, remain unpaid.
Accounts examined and found correct, E. and O. E.

| | |
|---|----------------------|
| FRANK T. KING,
A. P. HALLOCK,
DURAND WOODMAN. | } Finance Committee. |
|---|----------------------|

New York, December 22, 1893.

Reports from the secretaries of the New York, Rhode Island, and Washington Sections were read, reporting a good attendance and the presentation of numerous papers at the meetings.

The New York Section has allied itself with other scientific bodies in New York City forming collectively the Scientific Alliance. There is no amalgamation in this nor does the council of the alliance to which each society delegates three members have any control over the internal affairs of the constituent societies. The present membership is 147 a gain of fifteen during the year. Total expenses for the year ending October 6, \$88.60. Present officers, Peter T. Austen, chairman; M. Loeb, secretary and treasurer; A. A. Breneman, Wm. McMurtrie, and A. C. Hale, executive committee; P. T. Austen, Wm. McMurtrie, and J. H. Stebbins, delegates to the Scientific Alliance.

The Rhode Island Section reports an addition of one name to its membership making a total of seventeen members. Nine meetings were held from September 1, 1892, to July 1, 1893, at which numerous papers of interest were presented. The officers are, John Howard Appleton, Chairman; E. E. Calder, secretary-treasurer; and the chairman and secretary-treasurer, *ex-officio*, and Charles Catlin, executive committee.

The Washington Section. At the meeting of the Washington Chemical Society held May 11, 1893, the society voted to become a section of the American Chemical Society, and certain amendments to the constitution were presented to make it conform to such action. These amendments and a revised constitution were adopted December 14, which consummates the formation of the Local Section. No meetings were held between May 11, and October 31. The section has 94 members. The officers are F. P. Dewey, president; Cabell Whitehead and K. P. McElroy, vice-presidents; E. A. de Schweinitz, treasurer; A. C. Peale, secretary; F. P. Dewey, T. M. Chatard, K. P. McElroy, E. A.

deSchweinitz, A. C. Peale, H. W. Wiley, F. W. Clarke, Cabell Whitehead, and R. B. Warder, executive committee.

The Cincinnati Section presented no report. Since the meeting a report from the local secretary has been received which shows that the present membership is fifty-five a gain of seven. Eight meetings have been held at which numerous papers were read. The officers are: president, C. R. Stuntz; vice-presidents, W. Mumper and E. Twitchell; secretary, W. Simonson; treasurer, H. E. Newman; and directors, W. Dickore, J. U. Lloyd, A. C. Ramsay and E. C. Wallace.

The following papers were then read:

The Widespread Occurrence of Barium and Strontium in Silicate Rocks. *W. F. Hillebrand.*

The Estimation of Small Amounts of Barium and Strontium in Silicate Analysis. *W. F. Hillebrand.*

A Plea for Greater Completeness in Chemical Rock Analysis. *W. F. Hillebrand.*

A Study of the Distribution of the Oleo-resins in *Pinus Palustris*. *Oma Carr.*

Salicylic Acid in Food. *K. P. McElroy.* Read by title.

Utilization of Garbage. *Bruno Terne.* Read by title.

Adjourned at 2 P.M.

In the afternoon a visit was paid to the works of the Baltimore Copper Smelting and Rolling Company, under the guidance of members of the local committee. The raw material consists of Anaconda Matte which is worked up into copper by the ordinary method of roasting and smelting. The impure copper is then subjected to electrolysis and subsequently melted and cast. Another portion of the roasted copper oxide is boiled with sulphuric acid and the blue vitriol crystallized out and sold. Silver is separated by the addition of a small amount of common salt.

In the evening a dinner complimentary to the visitors was given by the local committee at the Eutaw House. Dr. Wm. Simon acted as toastmaster and H. W. Wiley, Wm. McMurtrie, Ira Remsen, F. W. Clarke, J. H. Appleton, Edward Hart, W. L. Dudley, and C. B. Dudley responded to toasts.

THURSDAY, DECEMBER 28.

Papers were read as follows:

Some Facts Relating to Type Writing Machine Oils. *Thomas Taylor.*

Report on the Determinations of Atomic Weights published during 1893. *F. W. Clarke.*

The Detection of Strychnine in an Exhumed Human Body. *W. A. Noyes.* Read by Edward Hart.

The Importance of the Study of Biochemistry. *E. A. de Schweinitz.* Read by C. E. Munroe.

Upon Uniformity in Sampling and Assaying Copper Bullion. *G. W. Lehmann.* Read by title.

The Preservation and Arrangement of Chemical Abstracts and Clippings. *Thomas M. Chatard.*

Historical Notes on the Electro-metallurgy of Zinc. *Charles Platt.*

The Phenylhydrazin Test for Glucose in Urine. *C. E. Pellew.* Read by title.

Expert Testimony. *W. P. Mason.*

The Boric Acid Springs of Tuscany. *W. P. Mason.*

Phosphorus in Steel. *C. B. Dudley.*

Some Points in the Volumetric Estimation of Phosphorus. *C. B. Dudley.*

Determination of Phosphorus by the Molybdate Method in Presence of Arsenic in Iron, Steel and Ores. *James O. Handy.* Read by C. B. Dudley.

The Analysis of Malt. *J. A. Miller.* Read by title.

Determination of Nickel in Steel. *Jos. Westesson.* Read by title.

Preliminary Note on Electrical Organic Analysis. *Edward Hart.*

Convenient Resistance Board for Use with Blackened Lamps. *Edward Hart.* Read by title.

After a recess of five minutes the secretary read a telegram of congratulation from A. B. Prescott, of Ann Arbor, Mich., as follows:

ANN ARBOR, MICH., December 26, 1893.

Prof. H. W. Wiley, or Secretary American Chemical Society,
Baltimore, Md., (Hotel Rennert).

"I rejoice with Society upon the results of ninety-three; the membership enrolled, the JOURNAL established, the organization effected and the congress of chemists overflowing, each an event in American Chemistry; an event international is Bolton's Bibliography of Four-Hundred Years. With regret that I must be absent,"

ALBERT B. PRESCOTT.

The secretary was instructed to make a suitable response.

The report of the committee of canvassers was presented showing the election of H. W. Wiley as president; A. C. Hale, secretary; C. F. McKenna, treasurer; F. E. Dodge, librarian; C. F. Chandler, P. T. Austen, C. A. Doremus and H. C. Bol-

ton as directors to serve two years. C. B. Dudley, C. E. Munroe, Wm. McMurtrie and J. H. Appleton to serve as councilors for three years.

H. W. Wiley, chairman of the committee on new charter, reported that he had been unable to obtain a meeting of the committee, but that on his individual responsibility he reported in favor of the surrender of the New York Charter and the organization of the society under a new charter to be obtained from Congress. At the suggestion of Dr. McMurtrie and C. E. Munroe the matter was referred to the council for further examination with power to act.

On motion of Edward Hart the president was authorized to appoint a committee of seven to include the members of the committee on papers and publications to act as an advisory board on matters pertaining to the "style" to be used in the JOURNAL. (nomenclature, spelling, punctuation, etc.). The president subsequently named the following persons to act as members of this committee: Edward Hart, chairman; J. H. Long, Edgar F. Smith, A. B. Prescott, G. C. Caldwell, T. H. Norton and H. Carrington Bolton.

On motion of J. H. Appleton a committee of seven was appointed to petition Congress for a more specific wording of that part of the tariff bill pertaining to importation of duty free apparatus and supplies for scientific work. The committee consists of C. E. Munroe, chairman; H. B. Nason, Edward Hart, E. F. Smith, J. H. Appleton, A. B. Prescott, and W. L. Dudley.

Dr. Wiley thanked the society for the honor done him in a re-election to the office of president. He believed, however, as the office of president was entirely honorary that two terms for one person was a mistake. As a mistake had now been made he felt bound to accept, especially as a declination to serve would put the council to inconvenience and delay business that should be attended to promptly.

Mr. C. F. McKenna offered his resignation as treasurer, stating that he found the work required so much time that he felt unable to longer attend to it. Referred to the council.

On motion of F. W. Clarke the thanks of the society were voted to the local committee of arrangements, to President D. C.

Gilman and Prof. Ira Remsen, of Johns Hopkins University, for courtesies extended, to the Baltimore Copper Smelting and Rolling Co., the Lazaretto Chemical and Fertilizer Co., and the Maryland Steel Co., for the privilege of inspecting their plants, and to Baker, Whitely and Co., and the Rasin Fertilizer Co. for transportation.

Adjourned.

In the afternoon the members visited the works of the Maryland Steel Co., at Steelton. The tugs Sea-Wall and Chicago carrying the party down the bay.

These works comprise four large blast furnaces, two twenty ton Bessemer converters and a complete ship building plant. A recent addition is the immense shears operated by hydraulic power which were used in lifting Krupp's gun from the vessel to the car upon which it was transported to Chicago. The party were taken through the works by Mr. Frank T. King and through the Bessemer Steel department by Mr. G. F. Knapp.

Local Committee of Arrangements.—C. P. Van Gundy, chairman; W. B. D. Penniman, secretary; Wm. Simon, W. J. Gascoyne, R. D. Coale, Chas. Glaser, G. W. Lehmann, A. R. L. Dohme, A. J. Corning, Wm. Glenn and G. A. Liebig, Jr.

REGISTER OF MEMBERS IN ATTENDANCE.

| | |
|---------------------|--------------------|
| Wm. McMurtrie, | W. F. Hillebrand, |
| Chas. F. McKenna, | G. L. Spencer, |
| P. Fireman, | H. B. Nason, |
| Walter B. Randall, | Wm. P. Mason, |
| Charles L. Parsons, | J. H. Appleton, |
| Chas. B. Dudley, | E. C. Franklin, |
| E. W. Allen, | Thomas Taylor, |
| W. D. Bigelow, | G. A. Chalmot, |
| H. W. Wiley, | W. R. Orndorff, |
| Edward Hart, | A. P. Sharp, |
| W. J. Gascoyne, | Charles Platt, |
| W. B. D. Penniman, | R. M. Parks, |
| A. L. Browne, | Sam'l P. Sadtler, |
| W. Liman, | Thomas M. Chatard, |
| C. P. Van Gundy, | H. H. Hawling, |
| Wm. Bromwell, | G. B. Pfeiffer, |
| Wm. Simon, | G. F. Barker, |
| A. R. L. Dohme, | Geo. Steiger, |
| R. D. Coale, | Robt. B. Warder, |

Chas. Glaser,
Wm. Glenn,
A. J. Corning,
Charles E. Munroe,
Eugene Byrnes,
Wirt Tassin,
August E. Knorr,
Oma Carr,
T. C. Trescott,
Wm. H. Krug,
F. W. Clarke,
W. P. Cutter,

T. R. Wolf,
H. B. Hodges,
Edgar F. Smith,
Wm. M. Groevsnor, Jr.,
W. L. Dudley,
G. W. Lehmann,
J. B. Littlewood,
W. N. Mumper,
John Johns,
Edgar Richards,
Marcus Benjamin,
Lyman B. Hall.

THE WIDE-SPREAD OCCURRENCE OF BARIUM AND STRONTIUM IN SILICATE ROCKS.¹

BY W. F. HILLEBRAND.

AMONG the mass of published analyses of igneous eruptive and metamorphosed eruptive rocks, those in which barium and strontium are noticed are few indeed, unless the work has been of a special nature, like that of Sandberger in the development of the lateral secretion theory. Yet the very numerous analyses of igneous eruptive rocks of all ages and kinds made in the laboratory of the United States Geological Survey during the past thirteen years, have shown that these elements are distributed widely and in considerable quantity, in the United States at least, and doubtless elsewhere.

The percentages of barium and strontium oxides when present are usually below 0.1 per cent. each, but higher amounts are by no means uncommon, and for certain districts seem to be the rule rather than the exception. Within the past year two series of rocks from Colorado and Montana have been analyzed, both of which are noteworthy for the high percentages of barium found in them. Of seven rocks constituting the Colorado series six held from 0.13 to 0.18 per cent. BaO, while in the seventh the percentage was 0.43. The SrO ranged from 0.07 to 0.13 per cent. for six, and was 0.28 per cent. for that one highest in BaO. Of thirteen geologically related rocks from Montana, embracing basic as well as acid and intermediate types, the range of BaO

¹ Read at the Baltimore meeting, December 27, 1893.

was from 0.19 to 0.37, with an average holding of 0.30 per cent. Three others of the same series contained 0.10 per cent. or less, while the seventeenth carried 0.76 per cent. BaO. The SrO ranged from 0.37 per cent. in the last instance to an average of 0.06 per cent. for the other sixteen.

In view of the above showing the question arises, why was not this general distribution sooner recognized? The answer is undoubtedly given by the statement that it has not been the custom among chemists to look for barium and strontium in analyses of the kind under discussion, and doubtless for the following reasons:

1st. A belief on the part of many that the two elements were absent from most rocks, this belief being based on the supposed rarity of the few rock-constituting minerals known to contain barium and strontium as noteworthy constituents.

2nd. Admitting the possibility of their presence in minute quantities, the unimportance as an aid to classification by the lithologist of the knowledge that a rock may contain a few hundredths of one per cent., more or less, of barium or strontium.

The unsoundness of the first argument has been sufficiently demonstrated by the data given above for rocks of the United States, which show likewise what serious errors may be incurred by neglect to test for the elements in question. Barium and strontium carrying minerals, sometimes with high percentages of one or both, are more common rock constituents than was formerly supposed.

With regard to the second point it may be said that if the present decade or the next may be unable to make use of the knowledge referred to, this will probably not hold true of the lithologists of a still later period—an argument perhaps equally applicable to other elements than barium and strontium.

Regarding a further reason why barium has undoubtedly often been overlooked, the reader is referred to the following paper.

THE ESTIMATION OF SMALL AMOUNTS OF BARIUM AND STRONTIUM IN SILICATE ANALYSIS.¹

BY W. F. HILLEBRAND.

IN testing qualitatively for barium and strontium in the course of analysis of natural silicates it has probably been the custom to rely upon the spectroscopic examination of the ignited calcium oxalate, on the assumption that, notwithstanding the well-known greater solubility of barium and strontium oxalates over the corresponding calcium salt, the latter would carry down enough of the former to render detection of barium and strontium by aid of the spectroscope a matter of no difficulty.

This assumption in the case of strontium is well founded as I have observed times without number, but it may be entirely fallacious in the case of barium. The twice precipitated calcium oxalate of the analyses marked "later" in the next following paper, affording a very strong spectroscopic reaction for strontium, but failed to give one for barium, although the oxide of this element was a constituent of the rocks up to 0.76 per cent., and simply because the latter had been entirely kept in solution by the large amounts of ammonium chloride present. This observation suggested at once an explanation for the apparent rarity of barium in the silicate rocks of the earth's crust, and opened up a field for investigation as to the best course to pursue in the separation and estimation of the three alkaline earth metals under the conditions generally prevailing in rock analysis, that is to say, great excess of calcium over barium and strontium in presence of magnesium and large amounts of sodium and ammonium chlorides.

Brief consideration sufficed to reject recourse to collective precipitation of the alkaline earths by ammonium carbonate because of the well-known incompleteness of such precipitation under the prescribed conditions.

It seemed better to seek a separation of barium at the outset. This conclusion was fortified by the results of experiments undertaken to ascertain the behavior of strontium under conditions similar to and differing from the above. A large number of experiments were made with calcium, strontium, and barium sepa-

¹ Read at the Baltimore Meeting, December 27, 1893.

rately, and then with mixtures of the former and either strontium or barium. The absolute amounts experimented with were kept low in order that the conditions usually obtaining in rock analysis might be as nearly as possible preserved. It was not for a moment expected that an exact method of separating considerable amounts of barium from either calcium or strontium would be discovered. The most that was hoped for was to work out a method suitable of application where relatively small amounts of strontium and barium occur with relatively large amounts of calcium. The outcome only in a measure fulfilled the hope raised by a few preliminary tests, but the results seem to be of sufficient interest to merit somewhat detailed description.

The precipitates were formed in ammoniacal solution at a boiling heat and were allowed to stand over night before filtering. They were washed but once or twice with cold water because of the very marked solubility of both strontium and barium oxalate in hot water, and even in cold water if the washing is prolonged. The filtrates were evaporated to dryness, ammoniacal salts were removed by heat, and after solution of the residue strontium and barium were precipitated as sulphates, the former after addition of alcohol. The sulphates were, when necessary, tested spectroscopically. The amounts of the different salts taken are purely arbitrary, except that the highest weights for BaO are the chemical equivalents of the highest for SrO.

FIRST SERIES.

| | Amount taken calculated as oxide. | | (NH ₄) ₂ C ₂ O ₄ ·H ₂ O,
amount in excess
of that required
for conversion of
total bases to oxalates.
Grams. | NH ₄ Cl
Grams. | Total bulk of solution.
Cubic centimeters. | SrO in filtrate. | |
|----|-----------------------------------|--------|---|------------------------------|---|-------------------------|-----------|
| | SrO | CaO | | | | Weight. | Per cent. |
| 1 | 0.0343 | | 1 | 10 | 250 | 0.0080 | 23.3 |
| 2 | 0.0343 | | 1 | 10 | 250 | 0.0045 | 13.1 |
| 3 | 0.0343 | | 2 | 10 | 250 | 0.0032 | 9.3 |
| 4 | 0.0343 | 0.0560 | 1 | 10 | 250 | 0.0036 | 10.5 |
| 5 | 0.0343 | 0.0560 | 1½ | 10 | 250 | 0.00275 | 8.0 |
| 6 | 0.0343 | 0.0560 | 2 | 10 | 250 | 0.0023 | 6.7 |
| 7 | 0.00384 | 0.0560 | 1 | 5 | 250 | 0.0003 | 7.8 |
| 8 | 0.00384 | 0.0560 | 1 | 10 | 250 | 0.0005 | 13.0 |
| 9 | 0.0010 | 0.0560 | 1 | 5 | 250 | Faint sp'tro'pic trace. | |
| 10 | 0.0010 | 0.0560 | 1 | 10 | 250 | " | " |

From the above it is plain (1-3) that, as was to be expected, strontium is incompletely precipitated by ammonium oxalate in slight excess and that its solubility is markedly lessened by increase of the precipitant. Furthermore (4-6), that calcium if present in quantity exercises a notable effect in promoting completeness of precipitation. Finally, that with very small amounts of strontium and a great excess of calcium the precipitation of the former is practically perfect in presence of a sufficient excess of ammonium oxalate, irrespective of considerable variations in the ammonium chloride. Additional experiments in which 5-6 grams of sodium chloride were added showed that this salt exercises a very slight but appreciable solvent effect on strontium oxalate. In entire absence of ammonium chloride on the other hand, precipitation of as much as 0.004 gram SrO is practically perfect in presence of 0.0560 CaO.

SECOND SERIES.

| | Amount taken
calculated as oxide. | | (NH ₄) ₂ C ₂ O ₄ · H ₂ O.
Amount in excess
of that required
for conversion of
total bases to oxalates.
Grams. | NH ₄ Cl
Grams. | Total bulk of solution.
Cubic centimeters. | BaO in filtrate. | |
|----|--------------------------------------|--------|--|------------------------------|---|------------------|-------------|
| | BaO | CaO | | | | Weight. | Percentage. |
| 11 | 0.0509 | | ↓ | 5 | 250 | 0.0230 | 45.2 |
| 12 | 0.0509 | | 1 | 5 | 250 | 0.0089 | 17.5 |
| 13 | 0.0509 | | 2 | 5 | 250 | 0.0070 | 13.7 |
| 14 | 0.0509 | | 4 | 5 | 250 | 0.0051 | 10.0 |
| 15 | 0.0509 | | ↓ | 10 | 250 | 0.0457 | 89.8 |
| 16 | 0.0509 | | 1 | 10 | 250 | 0.0243 | 47.7 |
| 17 | 0.0509 | | 2 | 10 | 250 | 0.0138 | 27.1 |
| 18 | 0.0509 | 0.0560 | ↓ | 5 | 250 | 0.0436 | 85.6 |
| 19 | 0.0509 | 0.0560 | ↓ | 5 | 250 | 0.0293 | 57.5 |
| 20 | 0.0509 | 0.0560 | ↓ | 10 | 250 | 0.0489 | 96.0 |
| 21 | 0.0509 | 0.0560 | ↓ | 10 | 250 | 0.0458 | 90.0 |
| 22 | 0.0509 | 0.0560 | ↓ | 10 | 250 | 0.0463 | 90.9 |
| 23 | 0.0509 | 0.0560 | ↓ | 10 | 250 | 0.0346 | 68.0 |
| 24 | 0.0509 | 0.0560 | 1 | 10 | 250 | 0.0206 | 40.5 |
| 25 | 0.0135 | 0.0560 | 1 | 5 | 250 | 0.0109 | 80.7 |
| 26 | 0.0135 | 0.0560 | 1 | 10 | 250 | 0.0106 | 78.5 |
| 27 | 0.00906 | 0.0560 | 1 | 5 | 250 | 0.0074 | 81.7 |
| 28 | 0.00906 | 0.0560 | 1 | 10 | 250 | 0.0079 | 87.2 |
| 29 | 0.00226 | 0.0560 | 1 | 5 | 250 | 0.00177 | 78.3 |
| 30 | 0.00226 | 0.0560 | 1 | 10 | 250 | 0.00197 | 87.2 |

In this series (11-17) the same action of precipitant and ammonium chloride that was observed in the first series makes itself manifest, only in much greater degree. Numbers 18-24 show in general the marked effect of small variations in the

amount of precipitant, although an exception may be noted in 22 when compared with 21. Comparison of 19 and 22 with 11 and 15 respectively shows that the presence of calcium exerts no retentive effect whatever on the barium, in marked contrast with its behavior toward strontium. With decreasing amounts of barium, the calcium remaining constant as well as the excess of precipitant, the slight influence of large variations in the ammonium chloride is apparent from numbers 25-30. The general result is to show conclusively that considerable amounts of barium may be separated almost completely from calcium by a single precipitation with ammonium oxalate in presence of considerable ammonium chloride, provided the precipitant is used in slight excess only.¹ Additional tests have shown that sodium chloride, as with strontium, slightly facilitates the separation from calcium; also that a double precipitation will effect the quantitative separation of over two mgms. BaO from fifty-six mgms. CaO under the conditions of experiments 29 and 30. In cases like the last the whole of the BaO has been recovered from the filtrates and from the calcium as nitrate no trace of barium could be separated by ether-alcohol. It goes without saying that by increasing the ammonium chloride still larger amounts of barium may be equally well separated, as has been proven by numerous tests.

In endeavoring to apply the knowledge thus gained to the separation of barium from both calcium and strontium, which is the problem usually encountered in silicate rock analysis, difficulties at once suggest themselves, namely, those arising from the partial solubility of strontium oxalate in ammonium chloride, from the presence of five to ten grams of fixed alkali salts, whereby the exact recovery of barium and the strontium that may have gone into solution with it is rendered much less certain, and furthermore, from the increased solubility of the oxalates of the calcium group when, as is very often the case, magnesium is present in some quantity.

Of several experiments made to test the degree of accuracy attainable, first in absence of sodium chloride, then in presence

¹ This fact was first observed by the writer in 1884, and was mentioned in a foot note to p. 592, appendix B., of Mr. S. F. Emmons' Monograph on the Geology and Mining Industry of Leadville.

of that salt and also of one of magnesium, thus reproducing the unfavorable conditions usually encountered in actual practice, the following will serve as fair examples.

1. CaO , 0.0560; BaO , 0.0023; SrO , 0.00095; $(\text{NH}_4)_2\text{C}_2\text{O}_4$, H_2O , one gram in excess, NH_4Cl , ten grams, total bulk of solution 250 cc. Two precipitations under precisely similar conditions. Found in filtrates, 0.00236 BaO , showing but the merest trace of strontium. Recovered from the lime, 0.00085 SrO holding fugitive spectroscopic traces of calcium and barium.

2. Precisely as in 1, with addition of $5\frac{1}{2}$ grams NaCl . In filtrates 0.0023 BaO , in lime 0.0006 SrO .

3. As in 2 with addition of 0.09 MgO . In filtrate 0.0023 BaO , in lime 0.0006 SrO .

It is apparent that the results are very satisfactory in 1, but that in 2 and 3 over thirty per cent. of the SrO has escaped detection although all the BaO was recovered. The amounts of both BaO and SrO taken in these tests exceed what is met with in the great majority of igneous eruptive rocks, and the error in SrO may therefore in most cases be disregarded, for after all an absolute error of twenty-five or even fifty per cent. in the estimation of a substance constituting only 0.1 per cent. of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

The procedure for the separation of the alkaline earth metals in silicate rocks as followed by myself with a fair degree of success for some time past, I will now outline, expressly premising, however, that it is not suitable for universal application, but that it seems to be the only one to meet the requirements of ordinary silicate analysis with anything approaching accuracy.

After a double precipitation, which should be made in any case, the ignited oxalate precipitate will contain nearly all the strontia and none of the baryta if the latter does not exceed 0.2–0.3 per cent. of the rock. If a larger quantity than 0.3 per cent. is present the precipitation by ammonium oxalate must be repeated or the rest of the barium subsequently separated from the strontium by ammonium chromate. The strontium is separated from the calcium by extracting the thoroughly dry nitrates (150–160° C.) by ether-alcohol, which is clearly shown by the

recent exhaustive researches of Fresenius¹ is the only one of the older methods at all capable of yielding a fairly satisfactory result. Hereby of course, any barium that might have been retained is also removed. The strontium weighed as sulphate should always be tested spectroscopically for barium, the barium sulphate likewise for strontium, either salt being brought into condition for making the test by reducing for a very few moments the whole or a part of the precipitate on a platinum wire in the luminous tip of the Bunsen burner, and then moistening with hydrochloric acid. If a trace of barium should be found with the strontium the error is insignificant and may be balanced by the strontium remaining with the calcium nitrate.

Before destroying ammoniacal salts, either by ignition or by nitric acid, prior to estimation of magnesia, a few drops of sulphuric acid should be added to precipitate the barium² which otherwise might contaminate the magnesium pyrophosphate. I say *might*, for small amounts of barium, up to 3 or 4 mgms. of oxide, will pass into the filtrate from the ammonio-magnesium phosphate. Only in exceptional cases have I ever found a trace of barium in the pyrophosphate after accidentally or purposely neglecting to effect a prior separation by sulphuric acid.

As to the barium itself it is improper to accept the amount thus separated from the magnesia as representing the total amount in the rock or mineral. It will almost always be found lower than the truth, probably for the reason that there are so many opportunities during the analysis for slight losses in the form of sulphate. Barium is best estimated in a separate portion which may also serve with advantage for the determination of titanium. The powder is decomposed in a capacious crucible with hydrofluoric and sulphuric acids, evaporation being repeated twice at least to ensure removal of all quartz. After volatilization of the excess of sulphuric acid the dry residue is digested with water containing several cubic centimeters of sulphuric acid to surely retain all titanium in solution, and a

¹ *Ztschr. anal. Chem.*, 29, 30, 32, 1890, 1891, 1893. Separation by amyl alcohol as recommended by P. E. Browning, *Am. J. Sci.*, 43, 50, and 314, 1892, has not been tried.

² The barium sulphate thus formed is not separated by filtration till after destruction of the ammoniacal salts, and, if this has been effected by nitric acid, not until after evaporation to dryness.

few drops of hydrochloric acid, and the solution is allowed to settle for some hours. The ignited insoluble matter is evaporated with relatively much sulphuric and a little hydrofluoric acid till the latter is removed and a clear solution results, which is then poured into a few cubic centimeters of cold water. The precipitate will now be free from calcium in all probability, but may contain a little strontium from traces of which it is easily freed by repeating once or twice the solution in strong acid and reprecipitation by water.¹ Unchanged weight after the final precipitation is evidence of purity of the barium sulphate, and the spectroscope should confirm this. These last mentioned manipulations require little expenditure of time even when they have to be repeated, and the result is usually eminently satisfactory. If the first weight of the barium sulphate is but one or two mgms. it is rarely necessary to purify the salt further.

Such is the procedure when only small amounts of barium and strontium have to be estimated. Should they be present in amount exceeding, say, two mgms. for SrO and four mgms. for BaO, or should with smaller contents a high degree of accuracy be desired, the already difficult analysis presents still greater difficulties. In such cases there remains no other way than to combine the barium and strontium found in the filtrates from the calcium oxalate with the strontium and barium separated from the oxalate itself, and to apply to the mixture the ammonium chromate method of separation as prescribed by Fresenius (*l. c.*). The practiced eye readily learns to judge by spectroscopic test of the ignited and weighed calcium oxide whether strontium is in sufficient quantity to necessitate this course, and the separate determination of barium as above described will decide with regard to that metal.

¹ If the rock happens to contain zircon this may, and probably will, remain with the barium sulphate until removed by appropriate means.

A PLEA FOR GREATER COMPLETENESS IN CHEMICAL ROCK ANALYSIS.¹

BY W. F. HILLEBRAND.

THE valuelessness to the mineralogist and geologist of many of the analyses of mineral substances made in earlier times is a fact too well-known to need substantiation. Defective methods of analysis, the difficulty of procuring pure reagents, and want of time for exhaustive examination have been largely responsible for this condition, but lack of appreciation of the fact, now so well established, that substances present in small amount may have an important bearing on the discussion of results, has no doubt contributed in no small measure to it.

Whatever the causes, the result has been the necessity for a vast amount of repetition in analytical work, and it behooves the present generation of chemists to heed well the warning and to work with a two-fold purpose in view, that of lightening the labors of those who come after us by enabling them to use our work with less supplementary examination, and of thereby enhancing our own reputations by meriting encomiums on work that has stood the test of time.

This monition applies to the lithologist as well as to the chemist, and the former should seek to make or have his analyses made as complete as possible, and not, as is so often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalies, and water; even going so far sometimes as to ask the chemist to omit tests for other constituents that may be present in small quantity for the sake of getting a greater number of more or less incomplete analyses accomplished. The latter, it is true, may serve the immediate purpose for which they were intended, but their incompleteness may on the other hand not only conceal points fruitful of suggestion to the attentive mind, but, what is of still greater importance, they may be actually misleading. Enough instances of total inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favor of greater completeness in rock and mineral analyses made for purely scientific purposes.

¹ Read at the Baltimore Meeting, December 27, 1893.

This is shown by the difference between the following analyses. The specimens were taken and analyzed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

| | Earlier
Analysis | Later
Analysis |
|--|---------------------|-------------------|
| SiO ₂ | 54.42 | 53.70 |
| TiO ₂ | | 1.92 |
| Al ₂ O ₃ | 13.37 | 11.16 |
| Cr ₂ O ₃ | | 0.04 |
| Fe ₂ O ₃ | 0.61* | 3.10* |
| FeO | 3.52* | 1.21* |
| MnO | | 0.04 |
| CaO | 4.38 | 3.46 |
| SrO | | 0.19 |
| BaO | | 0.62 |
| MgO | 6.37 | 6.44 |
| K ₂ O | 10.73 | 11.16 |
| Na ₂ O | 1.60 | 1.67 |
| Li ₂ O | trace | trace |
| H ₂ O below 110° C | | 0.80 |
| H ₂ O above 110° C | 2.76** | 2.61 |
| CO ₂ | 1.82 | |
| P ₂ O ₅ | | 1.75 |
| SO ₃ | | 0.06 |
| F | | 0.44 |
| Cl | | 0.03 |
| | <hr/> 99.58 | <hr/> 100.40 |
| Less O for Fl | | .19 |
| | | <hr/> 100.21 |

Another instance of a similar kind is given below. Here again certain differences are explainable by natural variations

* From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

** In the published analysis it does not appear whether this is total water, or, as seems probable, only that remaining above 100° C.

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in the proportions of the constituent minerals, but it can hardly be doubted that TiO_2 , BaO , SrO , P_2O_5 , and SO_3 , were present in both specimens in approximately the same amounts. In the earlier analysis in this case determinations of some supposed unimportant constituents were purposely omitted or only made qualitatively, with results which cannot be otherwise than fatal to a full comprehension of the mineralogical nature of the rock.

| | Earlier
Analysis | Later
Analysis |
|--|---------------------|-------------------|
| SiO_2 | 44.31 | 44.65 |
| TiO_2 | not est. | 0.95 |
| Al_2O_3 | 17.20 | 13.87 |
| Fe_2O_3 | 4.64 | 6.06 |
| FeO | 3.73 | 2.94 |
| MnO | 0.10 | 0.17 |
| CaO | 10.40 | 9.57 |
| SrO | | 0.37* |
| BaO | | 0.76 |
| MgO | 6.57 | 5.15 |
| K_2O | 3.64 | 4.49 |
| Na_2O | 4.45 | 5.67 |
| Li_2O | | trace |
| H_2O below 110°C . . . | 0.77 | 0.95 |
| H_2O above 110°C . . . | | 2.10 |
| H_2O by ignition | 3.30 | |
| CO_2 | | 0.11 |
| P_2O_5 | | 1.50 |
| Cl | | trace |
| SO_3 | | 0.61 |
| | 99.11 | 99.92 |

While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from my intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But I do maintain that in general the constituents which are likely to be present in sufficient amount to admit of determination in the weight of sample usually taken for analysis—say 1 gram for SiO_2 , Al_2O_3 , etc., to 2 grams for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative

* Not entirely free from CaO .

work, and their presence or absence noted among the results. If present in little more than traces that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavorable criticism when at some future time his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a thorough microscopical examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labor.

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH.

Received December 16, 1893.

FREUDENBERG published an article recently entitled "Über die Bedeutung der elektromotorische Kraft für elektrolytische Metalltrennungen" (*Zeit. für phys. Chemie.*, **12**, 97), in which are facts of great importance to all interested in the determination and separation of metals in the electro-chemical way. Some statements, however, have been made by Freudenberg to which I feel it my duty to reply. I discover upon p. 116, for example, these lines: "Auch gelingt eine Trennung (Kupfer) von Kadmium, welche bisher nur bei Gegenwart von Salpetersäure möglich schien, vortrefflich, wenn man die Lösung mit 10-20 cc. verdünnter Schwefelsäure versetzt und mit einer Spannung von 2 Volt elektrolysiert. Das Kupfer wird rasch und völlig kadmium-freigefällt." This very separation was carried out successfully three years ago by Smith and Frankel (*Am. Chem. J.*, **12**, 104-112 and *Ber. d. chem. Ges.*, **23**, Ref. 413) as will be observed from the literature references and the examples that follow:

1. To a solution containing 0.1975 gram copper and 0.1828 gram cadmium were added ten cc. of sulphuric acid (sp. gr. 1.09) and then 100 cc. of water. A current that liberated 0.3 cc. of electrolytic gas per minute acted upon the above mixture for twelve hours. The precipitated copper weighed 0.1968 gram.

2. A second experiment made under analogous conditions, except that the volume of sulphuric acid equaled fifteen cc. gave 0.1975 gram copper.

Freudenberg, while recognizing the fact that Smith and Frankel by electrolyzing solutions of metallic double cyanides effected many separations, seems not to be fully acquainted with all that has been achieved in this direction. Thus upon p. 113 he speaks of the separation of mercury from copper and alludes to the early statement of Smith and Frankel that if the quantity of copper exceeded twenty per cent. of the mercury the separation would not be satisfactory. This is true, but if Freudenberg had examined the literature that appeared later from this laboratory he would have found that Smith and McCauley (*J. Anal. Chem.*, 5, 489 and *Ber d. chem. Ges.*, 24, 2936) observed that "it is not only possible to separate these metals (mercury and copper) completely when present together in equal amounts, but even when the quantity of the copper is twice that of the mercury. In brief, the separation is as readily and accurately made as that of any other metal, *e. g.*, zinc from mercury. Furthermore, the presence of zinc, nickel, or other metals, in no wise, influences the separation of mercury from copper." I welcome, therefore, the results of Freudenberg's experiments with mercury and copper as confirmatory of those published by Smith and McCauley.

The observation of Freudenberg (p. 114) relative to the removal of gold when precipitated directly upon platinum will be found to be antedated by reference to *J. Anal. Chem.*, 5, 204.

As to the criticism made upon p. 117, in reference to the separation of bismuth from copper in the presence of potassium cyanide and citric acid I would only add that Smith and Frankel made numerous separations of these two metals in this way. Their results were highly satisfactory. It is true that

they never used quantities of bismuth exceeding 0.1 gram. The dishes in which the decompositions were made were large and offered ample surface so that the bismuth deposit was in every case satisfactory.

The separation of copper from arsenic, in ammoniacal solution, as outlined on p. 118 of Freudenberg's article, has already been successfully made by McCay (*Chem. Zeitung*, 14, 509) and by Smith and Frankel (*Am. Chem. J.*, 12, 428).

Again upon p. 122 Herr Freudenberg confirms an early observation made by Smith and Frankel in reference to their inability to completely separate cadmium from nickel in cyanide solution, but he is apparently ignorant of a later series of experiments by these same chemists in which they give proof that cadmium and nickel in cyanide solution can be separated in the electrolytic way if caustic alkali be added to the solution undergoing electrolysis. An example will illustrate:

A solution, containing 0.1723 gram cadmium, 0.1600 gram nickel, 2 grams of caustic potash, 2.5 grams of potassium cyanide to which 150 cc. of water had been added, was electrolyzed with a current that gave 2.2 cc. of electrolytic gas per minute. The precipitated cadmium did not contain nickel; it weighed 0.1723 grams (*J. Anal. Chem.*, 6, 87, and *Ber d. chem. Ges.*, 25, 784).

Freudenberg correctly adds on p. 124 that "Die Cyanverbindungen * * * * * haben jedoch unsere Trennungsmethoden bedeutend erweitert." This is evidenced by the many separations that have been effected in this laboratory in solutions of such compounds, *e. g.*

Cadmium from zinc, arsenic, tungsten, molybdenum, osmium, nickel, and cobalt; gold from palladium, platinum, copper, cobalt, zinc, and nickel; mercury from copper, zinc, nickel, cobalt, palladium, arsenic, tungsten, molybdenum, platinum, and osmium; and silver from copper, zinc, nickel, cobalt, arsenic, tungsten, molybdenum, platinum, and osmium.¹

UNIVERSITY OF PENNSYLVANIA,
NOVEMBER 10, 1893.

¹ *Am. Chem. J.*, 11, 352, 264; 12, 428; 13, 417; *J. Franklin Inst.*, Dec., 1889; *J. Anal. Chem.*, 5, 489; 6, 87.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY,
UNIVERSITY OF MICHIGAN.]

DETERMINATION OF NICKEL IN NICKEL-STEEL.

BY E. D. CAMPBELL.

Received December 21, 1893.

THE growing importance of nickel-steel has rendered it desirable to have a rapid and accurate method for the determination of nickel in that metal, since the value of the steel is largely dependent upon the amount of nickel which it contains.

The methods in use at present for the determination of comparatively small amounts of nickel in the presence of a large amount of iron, and the separation of the nickel from the manganese and copper, with which it is in most cases associated in this steel, involves usually one or more basic acetate precipitations and the use of either hydrogen sulphide or of ammonium sulphide in the subsequent work.

On account of the strong tendency of the basic acetate of iron to retain nickel, and of the various objections to the use of hydrogen sulphide or of ammonium sulphide as a precipitant, it was thought desirable, if possible, to devise a method which should not be open to any of the above objections.

The following methods worked out with my assistance by Messrs. Richard Fischer and W. G. Wallace, will, I think, be found to be sufficiently accurate for technical work. As the result of a large number of experiments upon solutions of steel, to which had been added known amounts of nickel, manganese and copper, the last two being added in amounts varying from two to ten times that in which they would occur in nickel-steel, in order that any interference of these elements might be detected, it was found that the nickel could be accurately determined within 0.001 gram, the usual error not exceeding 0.0003 gram to 0.0005 gram. The amount of nickel recovered is usually a little higher than the true amount, the increase being due to the solubility of ammonium manganous phosphate, the manganese of which accompanies the nickel in the subse-

quent work. The principles involved in the processes below described are the following:

1st. The iron is precipitated as ferric phosphate in cold, strong acetic acid solution, under which conditions it precipitates perfectly free from nickel, although retaining a small amount of copper.

2nd. The copper is separated from manganese and nickel in hydrochloric acid solution by means of granulated lead.

3rd. The manganese and lead, which displace the copper, are separated from the nickel by means of a cold ammoniacal solution of sodium phosphate.

4th. The nickel is determined in the ammoniacal filtrate from the phosphate of manganese and lead, by titration with standard potassium cyanide or by electrolytic deposition.

In case the nickel is accompanied by cobalt the latter metal remains with the nickel, and may be separated from it by any of the well-known methods after dissolving off the electrolytically deposited nickel.

The two methods described below are identical up to the point where a portion of the filtrate from the phosphates of manganese and lead is taken. The description of that part of the methods common to both will be first given, and then the two ways of treating the above filtrate for the final determination of nickel will be detailed.

DETAILS OF METHODS.

Take 2.2222 grams nickel-steel, place in a 500 cc. graduated flask, add twenty cc. nitric acid, sp. gr. 1.20, and five cc. strong hydrochloric acid sp. gr. 1.21. Boil until the solution is clear, which will usually require not more than from five to ten minutes. Remove from the plate and add 155 cc. sodium phosphate solution. If a slight precipitate should form which does not dissolve upon shaking, add carefully a few drops of hydrochloric acid until the solution clears up. Add twenty-five cc. strong acetic acid, sp. gr. 1.04 then 100 cc. sodium acetate solution, shake, dilute with water to 502.5 cc., shake again and allow to stand fifteen minutes. Filter through a dry, twenty-five cm. filter, catching the filtrate in a dry beaker. As soon as

enough of the filtrate has run through, which requires about ten minutes, draw off with a pipette 250 cc. of the filtrate, transferring to a number four beaker. This will give one-half of the solution, since it was found by experiment that the ferric phosphate from the amount of steel taken occupies 2.5 cc. Bring the solution to a boil and add twenty grams potassium hydroxide previously dissolved in forty cc. of water. Boil five minutes, then keep just below boiling point until the precipitate has settled and the solution is clear. This precipitates copper, manganese, and nickel so completely that the filtrate gives no color with hydrogen sulphide. Filter through asbestos, using a pump, decanting as much of the solution as possible before allowing the precipitate to get upon the filter. Wash with water. Dissolve the precipitate on the filter in a hot solution of six cc. strong hydrochloric acid with an equal volume of water. Wash the filter using only as much water as is necessary. To the solution in the flask, which should not exceed fifty cc. and should have a temperature of 40° to 50° C. add fifteen grams granulated lead and agitate at frequent intervals for five to ten minutes. This will completely precipitate the copper, a small amount of lead going into the solution. Filter through a small glass wool filter, catching the filtrate in a number two beaker; wash the granulated lead with a small amount of water and boil the solution down until it does not exceed sixty cc. Add ten cc. of sodium phosphate solution, then ammonium hydroxide until a precipitate just forms, then hydrochloric acid until the solution just clears up, cool until cold, and transfer to a cylinder or flask graduated to 111.1 cc. Add five cc. strong ammonium hydroxide, sp. gr. 0.90, dilute to the mark, shake well and allow to stand fifteen minutes. Filter through a dry nine cm. filter, receiving the filtrate into a dry beaker. Draw off, by means of a pipette, 100 cc. of this filtrate which is equivalent to one gram of the original steel, and treat by one of the two following methods:

I. ELECTROLYTIC METHOD.

Transfer the 100 cc. of filtrate above mentioned to a large platinum dish having a capacity of about 200 cc. Add twenty-

five cc. of strong ammonium hydroxide, sp. gr. 0.90, and dilute to 175 cc. Electrolyze for at least four hours, preferably over night, using a current yielding four cc. of electrolytic gas per minute. This strength of current can be easily obtained by connecting three medium sized cells. A very satisfactory arrangement to avoid the excessive loss of ammonia and the spattering of the solution due to the active evolution of gas, is to cover the platinum dish with a large watch glass perforated in the center through which the positive electrode, consisting of a large platinum cone, is suspended by means of a platinum wire.

The end of the precipitation of the nickel is indicated when a drop of the solution placed upon a drop of ammonium sulphide gives no color due to nickel sulphide. When the nickel is completely precipitated, disconnect the battery, wash the nickel thoroughly with water, then finally twice with alcohol and, after draining off as much as possible, heat for a few minutes in an air-bath at 110° C. Cool and weigh. After getting the combined weights of the platinum dish and nickel, dissolve off the latter by warming with 5-6 cc. of nitric acid, sp. gr. 1.20, then wash the platinum dish by means of water and alcohol and dry and weigh as before. The difference in the two weighings gives the nickel.

It is more satisfactory to weigh the empty dish after the precipitated nickel has been dissolved off than before electrolysis, since in this way a shorter time will elapse between the two weighings and consequently less error will be introduced from variations in atmospheric conditions. This latter source of error may be still further reduced by employing as a counterpoise for the platinum dish, upon which the nickel is precipitated, a similar platinum dish washed, dried and cooled under the same circumstances as the former.

2. VOLUMETRIC METHOD.

Take 100 cc. of the filtrate from the phosphate of manganese and lead, add hydrochloric acid very carefully until the blue color of the double ammonium nickel chloride disappears, then add ammonium hydroxide, drop by drop, until the blue just reappears and add an excess not exceeding one cc. Dilute to 200

cc., add five cc. of cupric ferrocyanide indicator and run in standard potassium cyanide until the solution turns from the purple color of the indicator to a perfectly clear light straw yellow. Subtract from the number of cubic centimeters of potassium cyanide used, the correction for the indicator. The difference gives the amount necessary to convert the nickel into the double cyanide of potassium and nickel. Multiplying this by the factor of the potassium cyanide, expressed in metallic nickel, gives the amount of nickel in one gram of the original sample.

SPECIAL APPARATUS AND REAGENTS.

500 cc. graduated flask with an additional mark at 502.5 cc.
250 cc. drop pipette. 100 cc. drop pipette.

Glass stoppered cylinder or flask graduated to 111.1 cc. The graduated apparatus should be carefully calibrated and compared before using.

Sodium phosphate solution, made by dissolving 200 grams of the ordinary crystallized disodium hydrogen phosphate in 1860 cc. of water. Ten cc. of this solution contain one gram of the crystallized salt, and it requires seventy cc. to precipitate one gram of iron as ferric phosphate.

Sodium acetate solution, made by dissolving 250 grams crystallized sodium acetate in 820 cc. of water. 100 cc. of this solution contain twenty-five grams of sodium acetate, which is a slight excess over that which is necessary to convert the nitric and hydrochloric acids to sodium nitrate and chloride, with the liberation of the corresponding amount of acetic acid.

Granulated lead is of the same quality as that used in assaying. In size it should be that which passes through a sieve with twenty meshes to the inch, but remains upon a sieve with forty meshes.

Before using, the lead should be washed with dilute hydrochloric acid (one part acid to two parts water) in order to dissolve any oxide that may be present.

Standard nickel solution. This may be made from chemically pure nickel by dissolving 2.5 grams nickel in fifty cc. nitric acid, sp. gr. 1.20, adding an excess of hydrochloric acid, evaporating on a water-bath nearly to dryness, then diluting to 1000

cc., one cc. equals 0.0025 gram nickel. Or it may be made from chemically pure nickelous chloride by dissolving six grams in water with the addition of a few drops of hydrochloric acid, and diluting to 1000 cc. This latter solution must be standardized. In order to do this, take thirty cc., place in a large platinum dish, add twenty-five cc. of strong ammonium hydroxide, dilute to 175 cc. and electrolyze as in the electrolytic method for nickel.

Standard potassium cyanide solution. Take twelve grams of chemically pure potassium cyanide, dissolve in water, dilute to one liter. This must be standardized against a standard nickel solution. Since the presence of ammonium salts interferes somewhat in the titration with potassium cyanide, necessitating the use of a slightly greater amount of potassium cyanide than would be required if there were no ammonium salts present, it is better that the potassium cyanide be standardized under the same conditions as are met in analysis. To standardize the potassium cyanide, take 15–20 cc. of standard nickel solution, add six cc. of hydrochloric acid, sp. gr. 1.20, ten cc. sodium phosphate solution, ammonium hydroxide until the solution turns blue and then five cc. in excess. Now add hydrochloric acid until the blue color of the double nickel chloride disappears, then again ammonium hydroxide until the blue just reappears, and an excess not exceeding one cc. Dilute to 200 cc., add five cc. cupric ferrocyanide indicator, and run in potassium cyanide until the solution changes from the purplish color imparted by the indicator to a perfectly clear light straw yellow.

Divide the amount of nickel in the standard nickel solution taken by the number of cubic centimeters of potassium cyanide used, less the correction for the indicator. The result will give the strength of the potassium cyanide expressed in metallic nickel.

Cupric ferrocyanide indicator. Take 2.5 grams of crystallized cupric sulphate, dissolve in twenty-five cc. of water, add to this a solution of ammonium oxalate until the precipitate first formed just redissolves, then dilute to 500 cc. Dissolve 2.5 grams of potassium ferrocyanide in 500 cc. of water, then slowly pour this solution into the cupric sulphate solution, stirring constantly

during the operation. This will give a deep purplish brown solution of cupric ferrocyanide which may precipitate partially on standing; but the precipitate so formed will be so fine that it will easily remain in suspension for a long time, upon shaking the bottle, thus insuring uniform composition. To find the correction for the indicator take 200 cc. of water, add 6-8 drops of ammonium hydroxide, then five cc. of indicator, taken after shaking the bottle well, and then run in potassium cyanide until the characteristic change of color is obtained.

Five cc. of cupric ferrocyanide of the above strength require from 0.15-0.2 cc. of potassium cyanide, one cc. of which is equivalent to 0.0025 of nickel. If a stronger end reaction is desired, ten cc. or even fifteen cc. of the indicator may be used and a suitable correction made.

Repeated analyses of steel have shown that the nickel may be determined, by the volumetric method, within from 0.0003 to 0.0005 gram of the true nickel content, duplicate determinations being made in three hours. The electrolytic method requires three hours to the time the solution is ready for electrolysis.

ANN ARBOR, MICHIGAN.
December 7, 1893.

PRELIMINARY REPORT OF THE COMMITTEE ON THE TARIFF.

THE COLUMBIAN UNIVERSITY,

WASHINGTON, D. C., January 15, 1894.

H. W. Wiley, Ph.D., Etc., Etc.,

President American Chemical Society,

Sir:—Your favor of January 5, 1894, announcing the appointment of the Committee on the Tariff, with the undersigned as Chairman has been received, and while from the nature of the case, it has not been possible to call the committee together for action, steps have been taken to secure information upon which to base our action.

We learn that efforts are being made to try and settle the question "What are philosophical or scientific instruments and prepa-

rations?" and in this particular we would call attention to the fact that in 1884 the Secretary of the Treasury referred this very question to the National Academy of Sciences, and that the Committee appointed by that body reported that an instrument is "philosophical," not in consequence of its special construction or function, but in consequence of the uses to which it is to be put, and that many instruments may be put both to uses which are philosophical and to uses which are purely industrial or commercial, it therefore appears to this committee that the terms "philosophical apparatus and instruments" should be held to cover all such instruments and apparatus imported for the purpose of improving natural knowledge. (*Rept. Nat. Acad. Sci.*, 66-67; 1885.)

From inquiry thus far of officials familiar with the operation of our tariff laws it appears that the difficulty in securing for educational institutions the full advantage of paragraph 667, page 47 of the Tariff of October 1st, 1891, arises from the fact that if dutiable articles used in commerce or the industries be admitted duty free for educational institutions the door is thrown open for the evasion of the law by those not entitled to the benefit of the Act.

It has been suggested by experts that this difficulty might be surmounted and that educational institutions might obtain that relief which Congress evidently intended they should have, by substituting for the present statute one providing that educational and other favored institutions be granted a rebate of duties on all dutiable goods and material consumed by them. In this case goods would be purchased directly from the "stock on hand" of dealers, or by advanced orders as heretofore, and when delivered the invoices would be accompanied by authenticated statements of the duties paid, which amounts would be returned on presentation of the statement to the Secretary of the Treasury or to his authorized agent. It is claimed that by this plan the delays now incident to purchase, and the difficulties arising from inconsistent appraisement will be remedied.

Your committee would respectfully ask that any who are interested in this matter should send their views and suggestions to the chairman of the committee and especially that they should

supply him with the particulars of any instances of failure of the act or inconsistencies in appraisements which may have come personally to their notice.

Respectfully submitted,

CHARLES E. MUNROE,
Chairman.

EXPERIMENTS ON THE ESTIMATION OF GRAPHITE IN PIG METAL.

BY FRANK L. CROBAUGH.

Received December 19, 1893.

THE determination of graphite in pig iron is often required. At furnace laboratories there is rarely time and equipment necessary to do this work by combustion. Appended are some details of experiments made in the search for a simple, yet accurate, method. In all cases counterpoised two 9 cm. filters were folded together and the filtration performed upon them. After partial unfolding and drying at a temperature not exceeding 100° C., (higher temperature chars paper after treatment) the excess of weight of the inner paper will be the weight of the graphite or graphite plus impurities. If now the paper containing graphite plus impurities (chiefly silica) be burned and the residual weight subtracted from the excess of weight of the inner paper, the difference may be graphite. Five grams of the same drillings were taken for each operation.

The metal contained 1.68 per cent. silicon. The washing in every instance was first with water and hydrochloric acid 1.1 sp. gr. until all iron was removed. The last washings were invariably with water. When there was intermediate treatment on the filter, it will be described with the experiment. In duplicate experiments, A and B, 125 cc. nitric acid, 1.135 sp. gr. was used as solvent and continued at gentle heat for one hour.

| | A | B |
|-----------------------------------|-----------------|-----------------|
| Weight graphite plus silica . . . | 0.2105 | 0.2500 |
| Weight of residual silica . . . | 0.0255 | 0.0658 |
| | <u>5)0.1850</u> | <u>5)0.1842</u> |
| | 3.70 | 3.68 |

The larger amount of silica in B is due to its standing at a gentle heat while A was being filtered. This strength nitric acid dissolves the most silicon according to Dr. Drown, but our experience has been that it separates on slight evaporation or on standing.

In duplicate experiments C and D, 60 cc. hydrochloric acid 1.1 sp. gr. was used as a solvent.

After complete solution 100 cc. of water was added to each and allowed to stand over night.

| | C | D |
|-----------------------------------|-----------------|-----------------|
| Weight graphite plus silica . . . | 0.3500 | 0.3489 |
| Weight of residual silica . . . | 0.1732 | 0.1721 |
| | <u>5)0.1768</u> | <u>5)0.1768</u> |
| | 3.53 | 3.53 |

The larger amount of silica separated rendered the burning of the graphite more difficult than in A and B. The amount of silica separated represents nearly all the silicon of the metal.

In experiment E, the solvent was 125 cc. nitric acid sp. gr. 1.135 added first, then immediately 12 cc. of Baker and Adamson's 40 per cent. hydrofluoric acid. Solution was perfect within five minutes at a gentle heat, after which the solution was boiled vigorously for five minutes longer, being constantly kept covered to prevent evaporation.

| | E |
|---------------------------------------|-----------------|
| Weight graphite plus silica | 0.1768 |
| Weight of residual silica | 0.0000 |
| | <u>5)0.1768</u> |
| | 3.53 |

It was thought that hydrofluoric acid would either cause more of the silicon to go into solution and remain there or volatilize it from the boiling acid.

Some glaze was taken from the beaker but no severe corrosion occurred in several treatments in the same beaker.

Intermediate washing with a mixture, one-third strong ammonia and two-thirds water, was made with the hope of dissolving any silica that might still cling to the graphite.

On burning the filter containing the graphite nothing was left in the crucible but some minute dark spots, (likely traces of

elements seldom estimated in pig iron) too slight to effect the determination in question. In experiments A, B, C, and D, I feared that the silica weighed with the graphite might be hydrated and thus give too high results in graphite.

Experiment E provided means for eliminating this objection by wholly freeing from silica. Thus far no attention has been paid to the extraction of combined carbon from the graphite, except as far as the solvents used would do this work, either by dissolving and retaining it, or evolving it. When the graphite of experiment E was washed with ammonia, after all iron was removed, brownish coloration appeared in the funnel tube during the first two washings which suggested combined carbon in some form dissolved in ammonia. The following experiments were all started exactly the same as was E. The washing will be described along with results given.

| | F | G |
|-----------------------------------|-----------------|-----------------|
| Weight graphite plus silica . . . | 0.1818 | 0.1800 |
| Weight of residual silica . . . | 0.0000 | 0.0000 |
| | <u>5)0.1818</u> | <u>5)0.1800</u> |
| | 3.63 | 3.60 |

Both F and G were washed with alcohol, ether, and ammonia in order. Each of the three washings brought the brownish coloration as noted in E.

| | H | I |
|-----------------------------------|-----------------|-----------------|
| Weight graphite plus silica . . . | 0.1820 | 0.1855 |
| Weight of residual silica . . . | 0.0000 | 0.0025 |
| | <u>5)0.1820</u> | <u>5)0.1830</u> |
| | 3.65 | 3.66 |

H was washed with ammonia only. Copious brown color came. I was washed with alcohol and ether only. Brown color came.

| | J | K | L |
|-----------------------------------|-----------------|-----------------|-----------------|
| Weight graphite plus silica . . . | 0.1878 | 0.1830 | 0.1790 |
| Weight of residual silica . . . | 0.0000 | 0.0000 | 0.0000 |
| | <u>5)0.1878</u> | <u>5)0.1830</u> | <u>5)0.1790</u> |
| | 3.75 | 3.66 | 3.58 |

J was also washed with alcohol and ether only. Brown color came. K was washed with alcohol, ether, and ammonia, in or-

der named as were F and G. It was observed that more color came with ammonia than with alcohol and ether. The alcohol-ether and ammonia filtrates of K were preserved and will receive attention later. L was washed with ammonia, alcohol, and ether in order. Scarce a trace of color came with alcohol and ether.

In none of these experiments except I, was any residue left in the crucible except the dark spots previously alluded to, (soluble in boiling hydrochloric acid sp. gr. 1.20) and in that case, residual silica, showing that ammonia may be necessary to dissolve the last traces of silica, but not always necessary as proven by J.

From a comparison of results and character of washings, it is evident that ammonia is certainly as efficacious a wash as alcohol and ether for removing combined carbon or its compounds, and that where ammonia is used, alcohol and ether are unnecessary. The variation of the hydrofluoric acid results is not so great as to be inadmissible from a commercial standpoint.

This variation may be due to errors of manipulation, or to small graphitic crystals or nuggets crumbled rather than drilled from the pig and larger than the remainder of drillings thus rendering the sample of drillings not homogeneous.

These interlaced spongy particles of graphite, sometimes three mm. on a side are often noticed after solution of pig in 1.135 sp. gr. nitric acid. It may also be due to small amounts of fine graphite penetrating the inner paper and being retained by the outer paper or penetrating it also.

This phenomenon is sometimes noticed especially where retained by the second paper thus giving a dark color. Finally the chemical or mechanical action of the filtration may have disturbed the equality in weight of the two papers. Why then setting aside these sources of error and the dark spots on the crucible are we not weighing pure graphite, if the analysis be conducted as typified in experiment E? This modus operandi is shorter and free from the perplexities of the caustic potash method of Karsten. The alcohol-ether filtrate from K was evaporated to gentle dryness and formed a black mirror-like residue on the beaker, completely soluble in the ammonia wash

when warmed gently. The residue from the ammonia filtrate presented the same appearance but was not soluble in alcohol and ether, but readily taken up by ammonia.

Both filtrates on evaporation threw out the dissolved matter in brownish flocks. We hope to investigate this point more thoroughly and also the action of ammonia on the total carbon of pig iron as obtained by use of the double chlorides. Such work may aid in obtaining a better knowledge of the forms of combination of carbon with iron and the forms in which it is separated under different conditions.

Attention will also be paid to the character of spots on the crucible, but these would not be common to all pig iron and might exist to a greater extent in some than in others. I may note in conclusion that all filtrations were performed by aid of the pump, and that more closely concordant results might have been obtained had the filtrations been performed upon asbestos. It would also be interesting to determine whether the silicon of the metal under this treatment is volatilized or largely in solution.

LABORATORY OF STEWART IRON CO., L'T'D.,
SHARON, PA., DECEMBER, 1893.

THE DETECTION OF STRYCHNINE IN AN EXHUMED HUMAN BODY.¹

BY W. A. NOYES.

PROFESSOR T. G. Wormley in his book on the Micro-Chemistry of Poisons states that strychnine has never been found in an *exhumed* human body after a longer period of burial than forty-three days. His authority is the Ann. d'Hyg., April, 1881, 359. I have not been able to find in any chemical journal a contradiction of this statement, though there is a statement in the old edition of *Watt's Chemical Dictionary* which seems to be inconsistent with it. Under these circumstances the following account of a recent toxical case may be of some interest.

On April 26th of this year Drs. W. L. Athon and O. Mitchell, of Marshall, Ill., brought to me for examination the stomach, liver and a portion of the intestines of a child who died on June

¹Read at the Baltimore Meeting, December 28, 1893.

23rd, 1892, and was buried the following day. The body was exhumed on April 25th, 1893, after a burial of 308 days. The material submitted for examination weighed 505 grams. About fifty grams were examined for arsenic and other mineral poisons with negative results. About 350 grams of the remainder were extracted with dilute sulphuric acid and alcohol by the usual methods. The aqueous residue which remained on concentration of the alcoholic solution contained a considerable amount of oily matter which was separated by filtration and washed as thoroughly as possible. This residue (A) is usually considered to be nearly free from alkaloids but it was further examined as described below.

The filtrate, after concentration, treatment again with alcohol etc., was rendered alkaline with caustic soda and extracted with chloroform. The chloroform left, on evaporation, a considerable amount of oily bases which were partly volatile, as was shown by their fumes with hydrochloric acid. To separate the strychnine from this residue it was heated on a water-bath with a little concentrated sulphuric acid for two hours. After neutralizing the acid, the solution was extracted with chloroform. The residue obtained, was treated again in the same manner, and that residue, again. Stoehr¹ has shown that when pure strychnine is heated to 100° with pure concentrated sulphuric acid, for some time, it is completely converted into the mono-sulphonic acid. Apparently in the presence of much foreign matter and with a small amount of acid in an open watch-glass a considerable portion, at least, of the strychnine escapes this action of the acid. In any case, a portion of the last residue referred to above gave with potassium pyrochromote and sulphuric acid the violet color, changing after a short time to an onion red, which is characteristic of strychnine. While the use of concentrated sulphuric acid is open to objection and should never be resorted to when it is possible to avoid it, I do not know of any other method which would be successful in the case of such residues and such minute amounts of strychnine as were obtained in this case.

The oily residue (A) was treated with some purified ligroin,

¹ *Ber. d. chem. Ges.*, 18, 3429.

and very dilute sulphuric acid and the mixture was filtered with the aid of a pump in such a manner that both acid and ligroin were drawn through the filter. The acid solution and the ligroin were then separated and the strychnine was recovered from the solution and purified essentially as before. A considerably larger amount was obtained from this portion than from the first. The strychnine obtained was identified by the characteristic reaction with potassium pyrochromate and sulphuric acid, by the intensely bitter taste, by the crystalline form and double refraction as seen with the microscope, by the crystals obtained from the chloride with potassium chromate, and by the effect of about $\frac{1}{10}$ of a milligram upon a frog weighing about two grams. The frog died from the effects of the poison, the symptoms of tetanus being fully developed within ten minutes after the dose was administered. The crystals of the chromate were chiefly of the branching forms; there was a little evidence of octahedra but they were not positively identified. The branching forms, however, developed the characteristic violet color when touched with concentrated sulphuric acid.

The total amount of strychnine recovered was estimated to be about two milligrams.

In the trial, the chemical evidence was not contested. The defendant was, however, acquitted on other grounds.

ROSE POLYTECHNIC INSTITUTE,
DECEMBER 23, 1893.

NOTES ON DETERMINATION OF NICKEL IN STEEL.¹

BY JOSEPH WESTESSON, CHEMIST TO THE WASHINGTON NAVY YARD.

THE desirability of being able to determine nickel in steel by means of a shorter process than the one, now mostly in use, gave me cause some time ago, when a number of samples from nickel-steel plates were submitted for analysis to the ordnance laboratory, and when the tediousness of the said process became particularly apparent, to make some investigations in order to find a more direct method, and I shall beg permission to mention in a few words, what my trials led to.

In the process, above mentioned, the nickel is precipitated

¹ Read by title at the Baltimore meeting, December 28, 1893.

by means of hydrogen sulphide in the acetate solution, obtained by separating iron from nickel; the sulphide is filtered off, dried, ignited, dissolved in aqua regia and converted into the double sulphate with ammonia in order to obtain a suitable solution for electrolysis.

It occurred to me, that there ought to be some way, by which the nickel could be electrolytically precipitated *directly* in the acetate solution, and thus that part of the procedure, embracing the precipitation with hydrogen sulphide, entirely eliminated. If this could be done, it is evident, that there would be quite a saving of time, besides doing away with an unpleasant feature of the method. It became, therefore, my aim to simplify the old method in this peculiar part.

Now, as the presence of chlorides will prevent the electrolysis of nickel, and as the separation of the iron from nickel always had taken place in a chloride solution, I decided to bring my original solution into the shape of sulphates and then proceed on the old lines. After having made a number of more or less successful trials, I finally came to the conclusion, that the following method would answer the purpose very well:

One gram of the sample is dissolved in twenty cc. of sulphuric acid of 1.16 sp. gr., and the solution kept boiling for some time, whereupon five cc. of weak nitric acid is added in small portions. The solution is now evaporated until all the nitric acid is expelled, allowed to cool, water added and heated until clear. Neutralization with carbonate of soda is done in the usual way, but care should be taken not to carry it too close to the point of neutralization. Add water so as to make the bulk 375-400 cc. and precipitate with acetate of soda; filter into a casserole and evaporate the filtrate over a moderate flame; redissolve the ferric precipitate and repeat the precipitation twice, taking care not to make the bulk more than 400 cc. each time, and adding each filtrate to the first one. When the filtrates have been evaporated down to 400 cc., add ten cc. of concentrated ammonia and boil for a few minutes. The manganese will then settle out, evidently as $\text{H}_2\text{O}, \text{MnO}$, and is filtered off, whereupon the filtrate is ready for electrolysis. If the ammonia should be added to the concentrated filtrates, when *cold*, the manganese

will not separate out but will interfere considerably with the electrolysis later; it will in that case not only settle out at the anode, but will in fact contaminate the nickel on the cathode, not as loosely settled dioxide but alloyed with the nickel. When on the other hand, the manganese is precipitated by ammonia in the hot solution, the nickel is to a small extent carried along with the manganese, but I have in all my experiments never found the nickel, lost in that way, amount to more than one to one and a half per cent. of the amount of nickel present in the steel.

How this modification of the old process compares with the original a few results will show.

In a nickel-steel, containing 3.50 per cent. nickel, determined by the old process, the amount found by the modified process in five different analyses was: 3.42 per cent.—3.51 per cent.—3.48 per cent.—3.51 per cent.—3.43 per cent., and in another steel containing 0.19 per cent., the following amounts were found: 0.18 per cent.—0.19 per cent.—0.19 per cent.

The time necessary for analysis of this kind I have found to be about eight hours. Thus, if the analysis is commenced at 8 A.M. the solution will be ready for electrolysis at twelve o'clock, or before; with seven or eight Grove cells in good condition the analysis should be concluded at 4 P.M. I have invariably commenced at noon and left my cylinder over night on four Grove cells, the separation of iron from nickel being completed about four o'clock, or sometimes a little later.

A CORRECTION.

BY H. L. PAYNE.

Received January 29, 1894.

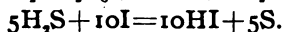
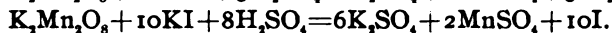
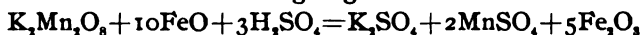
IN the *Journal of Analytical and Applied Chemistry* for September, 1892, 6, No. 9, I published 'A method for the Preparation of a Standard Iodine Solution,' and on page 482 I have taken the molecular weight of two atoms of iron as 128 instead of 112. This singular error which vitiates the entire calculation following it, has been called to my attention by several readers and I desire to correct the mistake and again call attention to the method itself. If any one has been unfortunate

enough to take the figures just as I gave them, he has no doubt been disappointed with the method. To such I make a humble apology and ask that they try again using the following changes.

The relation between the iron and the sulphur value of a permanganate solution is 112 to 32 or 7 to 2 instead of 8 to 2 and of a phosphorus permanganate solution with an iron value 6,141,285 cc. should be taken to make one liter of iodine solution titrating 0.01 per cent. S on five grams iron, instead of 325.7 cc.

To make the whole matter clearer I may state the process of computation in a more general form making use of the atomic weights 56.00 for Fe and 32.06 for S. To make an iodine solution titrating exactly 0.0001 gram S per cc.—0.01 per cent. S per cc. on one gram of substance taken—divide 349.34 by the iron value, *i. e.*, the grams per liter or milligrams per cc., of the permanganate solution to be used. This gives the number of centimeters of such a solution to be used in making one liter of iodine solution. If more than one gram of substance is taken, multiply the number accordingly; thus for a permanganate solution whose iron value is 0.005 gram Fe per cc., take 69.87 cc. to one liter, or if five grams of iron or steel be used in the sulphur determination, take 349.34 cc. per liter.

The reactions in the foregoing method are as follows:



therefore $\text{K}_2\text{Mn}_2\text{O}_8 = 10\text{Fe} = 10\text{I}_2 = 5\text{S}_8$,

or $2\text{Fe} = \text{S}_8$.

I hope now that this method has been correctly presented to the readers of THE AMERICAN CHEMICAL JOURNAL, that it will be made of the service which I believe its simplicity and accuracy deserves. I have tried it for over three years and have never had the slightest trouble.

CITY LABORATORY,
CLEVELAND, OHIO.

A RAPID AND ACCURATE METHOD OF DETERMINING THE MOISTURE AND OIL IN LINSEED CAKES AND OTHER FEEDING STUFFS.¹

BY A. P. AITKEN, D.Sc., CHEMIST TO THE HIGHLAND AND AGRICULTURAL SOCIETY OF
SCOTLAND.

IT frequently happens that when the same sample of linseed cake is analyzed by different chemists very considerable differences occur in the proportions of oil and moisture found by them.

The explanation of these discrepancies is to be found, not only in the different methods employed, but also in the inconstancy of the results obtained by the same method.

Determination of Moisture.—As regards the determination of moisture, the common practice in this country is to expose one or two grams of a finely ground sample in a water-bath for two hours and to regard the loss of weight as the measure of the moisture. A recent examination of this method has shown me that it may be very inaccurate and that uniform results cannot be obtained by it.

The amount of heating which a sample gets in an ordinary water-bath during two hours may not be sufficient to deprive it of all its moisture. The temperature within the bath is not constant and it is always below 100° C. The temperature of the external air, the amount of ventilation, the frequency with which the door is opened, the quantity of the sample used, the nature of the vessel containing it whereby a greater or less amount of surface is exposed to the current of hot air, are all fluctuating conditions. Moreover, in the case of linseed cake the sample continues to absorb oxygen during the whole time of its exposure in the bath and it does so the more rapidly the higher the temperature and the greater the surface exposed.

It thus happens that when a sample of finely ground linseed cake is exposed in a water-bath it goes on losing weight from loss of moisture for a time and thereafter gains weight from ab-

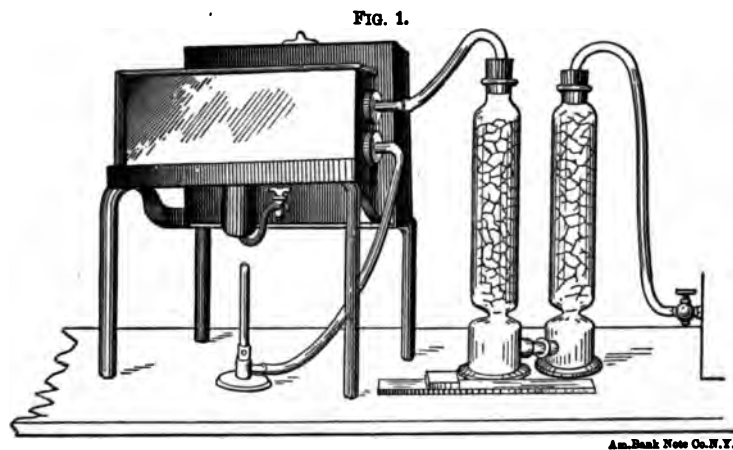
¹Read before the World's Congress of Chemists, August 22, 1893.

sorption of oxygen. Therefore, the time at which the sample ceases to lose weight is not that at which the sample is dry but only the time at which the loss of moisture and the gain of oxygen counterbalance each other.

In order that the sample may be thoroughly dried and that it may at the same time suffer no oxidation, it must be dried in an atmosphere from which air is excluded. An atmosphere of hydrogen is excellent for the purpose, but one of coal gas does quite as well and it is most readily obtainable. I have used coal gas for the purpose for some years and it is used also in some of the continental laboratories.

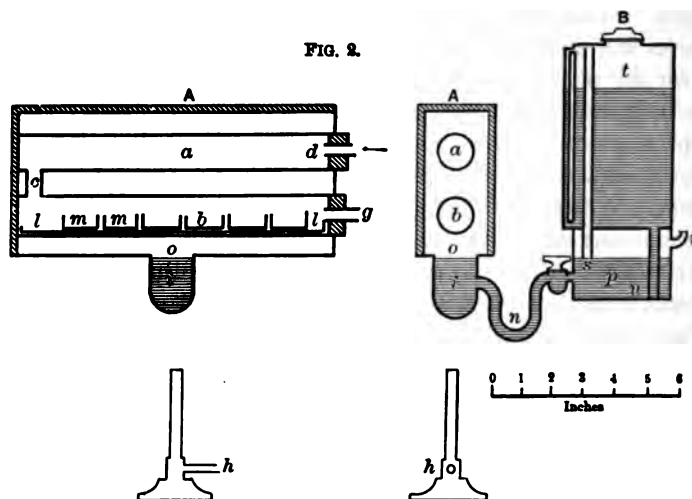
The apparatus I am about to describe secures that the sample is dried exactly at the temperature of boiling water and is so constructed that the coal gas is heated to that temperature before it comes in contact with the sample. It may be made of any dimensions, but the size which I prefer is that described below and capable of drying eight samples in an hour and a half.

The apparatus consists of a small rectangular box, ten inches long, four inches deep, and two inches wide, placed on edge as shown in Fig. 1, and in sections longitudinally and transversely, Fig. 2, A.



Through the box from end to end pass two hollow cylinders made of telescope tubing, and soldered into the box at each end.

The box is simply a steam-bath to heat the two tubular chambers, which are fitted at one end with the perforated cork and have the other end either closed with corks or entirely soldered up as in the diagram. The upper tubular chamber *a* is for heating the gas, and the lower one *b* for drying the samples, which are contained in little aluminum boats *m m* resting on a carrier of brass *l l* which slides into the chamber.



These boats, capable of holding one or two grams of cake, weigh only about one to two grams each, and are, therefore, very well adapted for weighing small quantities. The gas from the tap is led first through two drying bottles, filled, one with soda-lime and one with chloride of calcium, and enters the apparatus by the tube *d* in a perfectly dry state. It passes along the upper chamber *a*, where it is heated, and then through *c*, which is a tube connecting the upper and lower chambers. It arrives at the lower chamber *b* both hot and dry and passes along, drying on its way the samples (usually one gram each) contained in the little aluminum boats *m m*, eight of which can be accommodated on the carrier. The gas leaves the apparatus by *g*, and may be burnt there, but as the flow of gas is sufficient to keep a small Bunsen going, I connect the tube *g* with the Bunsen *h*.

The flame of this little Bunsen keeps the water in the thimble-

shaped cup *i* briskly boiling. The water in the thimble (about 1-2 ounces) is kept constantly at the level *o* by its connection with the automatic cistern B connected with the bath by the tube *n*, which is bent downwards and up again so as to prevent hot water from passing back into the lower section of the cistern *p*. As soon as the level of the water in this lower section falls below the mouth of the tube *s*, a bubble of air passes up the tube into the upper cistern *l*, and a corresponding quantity of water flows into the lower section through *u*, and restores the level of the water. A small hole *v*, into which an upwards bent tube is fitted, allows air to enter the lower section. The object of the upturned tube is to prevent water from spilling out of the air-hole, when the apparatus is carried about. This cistern contains more than a day's supply of water, and gives no trouble, and is supported along with the bath, on a light iron frame as shown in Fig. 1. The inside of the bath is thus constantly full of steam, which escapes by a hole at the top about $\frac{3}{16}$ of an inch in diameter. The bath is made of copper, but its entire surface is protected against contact with the surrounding air by means of asbestos sheeting $\frac{1}{8}$ inch thick.

The temperature in the upper chamber is thus kept constantly at the boiling-point of water, and not several degrees below it, as is usually the case in even the best water-baths. By means of this small apparatus, eight one-gram samples of cake can be dried within two hours. They are removed by drawing out the carrier, transferred to an exsiccator, and weighed in the aluminum trays, whose weights are known and deducted, thus giving the moisture. The results are perfectly accurate, and the cost in gas is very small—only about one cubic foot per hour.

The samples are now ready to have their oil extracted and estimated.

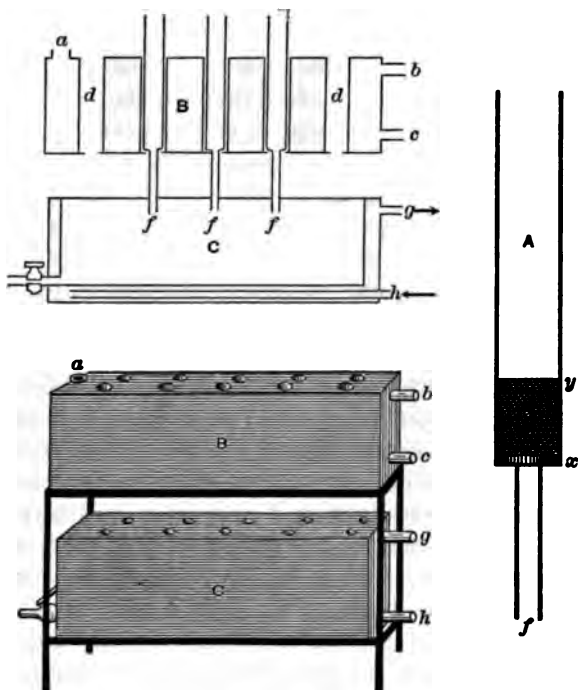
It is not essential that the last traces of moisture should be removed before the oil is extracted. If the sample is dried for half the time required to completely dry it, it is in a suitable condition for oil extraction. Nine-tenths of the moisture will have gone by that time, and the presence of about one per cent. of moisture does not appreciably affect the amount of oil extracted.

I prefer to take the samples whose moisture I have estimated, and which are completely dry, because I have a method of extracting oil by which even very small quantities of oil can be accurately estimated, and which possesses the further advantage of being more rapid than any other method that I know of.

Solvent for Oil in Cakes.—Ether, bisulphide of carbon, or benzene, are the solvents usually employed, but as ether is the one which is most common, most rapid, and most comfortable to work with, I prefer it to the others. It is a little more expensive, but the quantity used in oil determinations is small; the additional cost is more than compensated by the advantages mentioned. Ordinary pure ether, as supplied by wholesale chemists, having a specific gravity of 0.73, is sufficiently pure and dry for the purpose of oil extraction; but as most of the ether used is recovered by redistillation in the laboratory and may contain water, it must be dried before being again used. This is sufficiently accomplished by shaking it up with chloride of calcium repeatedly for some days, and redistilling.

Determination of Oil.—The oil may be determined either by directly weighing the oil extracted, or by weighing the dried substance before and after the oil is extracted, and determining the oil by the difference of the two weighings. There are two objections to the former method. In the first place, the flask in which the oil is caught is itself very heavy and presents too great a surface; and in the second place, the evaporation of the residual ether in the drying chamber takes a long time, and the surface of the oil becomes covered with a thin pellicle due to oxidation. The latter method is much to be preferred if a suitable apparatus can be had for doing the work simply and rapidly. The apparatus I have devised for that purpose is very simple, and is shown in Fig. 3. It consists of a set of brass tubes, polished smooth inside, see Fig 3, A, which is half the actual size, and is represented as charged with the dried sample. In charging the tube, the first thing required is to drop into it a small disk of wire gauze *x*, and then to insert a single or double wad of filter-paper, which is cut to fit the tube tightly, and pushed home with a ramrod. (I use a cork borer of the proper size for cutting the wads, and a piece of glass rod flattened out at the end

while hot, as a ramrod.) The object of the wire-gauze disk is to facilitate the flow of the ether through very fine powders, such



as ground grain, and also to enable the sample to be removed from the tube more easily after the oil is extracted. In the case of oil cakes the wire-gauze disk may be dispensed with.

The sample is then poured in through a little metal funnel whose neck just fits the extraction tube. Any powder adhering to the funnel is brushed in with a camel-hair brush, then another wad *y* is patted in on the top of the sample, carrying with it any powder that might have adhered to the side of the tube and leaving the upper part of the tube clean and bright. The tube is now put into one of the holes in box *B*, which is simply a warming box made of zinc, shown also in section.

The holes *d d*, etc., are tubes which pass through the box from top to bottom, and are made a shade wider than the ex-

traction tubes, which should drop in easily. As soon as the extraction tubes are filled they are dropped into these tubular openings, which are provided with a ledge at the base to sustain the extraction tubes.

Hot water is poured into the box at *a*, or a constant current of hot water may be made to flow through the box, entering at *b* and flowing out at *c*, by attaching these by means of tubes to a copper coil under which a Bunsen is burning at a safe distance. At first I used the circulation method, but now I prefer to have no gas burning anywhere near the extractor. It is quite convenient to supply hot water at *a*, and withdraw the cooled water at *c* from time to time. As soon as the extractor tubes are dropped into their places, ether is poured into them to within an inch of the top, and by the time that the five tubes are thus filled the ether will be boiling in the first tube. A cork is now firmly fixed into each tube in succession, thus preventing the ether-vapor from escaping, and the presence of the confined vapor, forces the boiling ether down through the samples and out through the lower opening *f* into little bottles placed beneath, so that the oil may be collected from each tube separately. If the oil of each tube is not to be kept separate, the mouths of the extractor tubes are made to dip into a zinc box *C* beneath, through small holes on the top, and there the oily ether collects and is run off from time to time, and redistilled for future use. There is considerable loss of ether by this method, but that is much reduced as one becomes expert in handling the apparatus; and if the other box below is provided with double walls between which a current of cold water is kept flowing through the openings *g*, *h*, the loss from evaporation is still further reduced.

This process of filling the tubes with ether is repeated ten, fifteen, or even twenty times, according to the difficulty of extracting the oil. The operation is complete when a drop or two of ether, falling from the exit *f* towards the end of an extraction, is caught on a clean watch-glass and evaporated without leaving any residue. The extractor I use in my laboratory is fitted for ten tubes, and after a little practice the oil from the ten samples of cake can be extracted with it in one hour. The extraction of oil from a sample, by means of Soxhlet's apparatus, which is the

one chiefly used at present, takes about five hours, so that this little apparatus has a great advantage over it as regards speed; but many comparative tests have proved that it also has the merit of making a more thorough extraction of oil. This is due to the fact that the extraction is made with boiling ether, and that no oily ether that has once been washed through is able to run back upon the sample again, as is the case with Soxhlet's apparatus. In extracting the oil from some substances, such as grain or other starchy powders, the resistance to the passage of ether is so great that even a tightly-fitting cork is apt to be blown out by the pressure of the vapor. In such cases I use caps with a cork washer inside, which fit on to the top of the tubes with a screw of half a turn which is very rapidly adjusted.

When the oil has been completely extracted, the removal of the sample is a neat and easy operation. It is done by inserting the cut end of the glass ramrod into the opening *f* and slowly pushing out the sample (wads and all) into a weighed aluminum capsule. The wads are now removed, after brushing off any particles of powder adhering to them with a camel-hair brush, and the dry powder, after exposure for a short time to a temperature of 100° C., is cooled in an exsiccator and weighed. The difference between that and the former weighing, is the weight of the oil extracted.

It is evident that the accuracy of the oil determination by this method depends upon the accuracy of the determination of the moisture; but as by the method above described the moisture can be accurately determined, there is no danger, if that method is adopted, of making any error in the estimation of the oil. In estimating moisture in the ordinary way it is considerably underestimated, usually to the extent of one-twentieth or more, and in such circumstances that which is underestimated in the moisture is usually added to the oil; for the common practice is to determine the percentage of moisture in one part of the sample, the percentage of moisture and the oil together in another, and to subtract the former from the latter, so as to give the percentage of the oil.

It thus happens that in the analysis of an ordinary linseed

cake differences of two or even three per cent. are not unusual in the percentage of oil found by different analysts.

I have submitted this method to a long series of tests in my laboratory during the past winter and I have been so satisfied with the accuracy and uniformity of the results obtained by it and with the simplicity and rapidity of the whole process that I cordially recommend it to agricultural chemists in America and especially to those who have small laboratories and a large number of samples to analyze.

The apparatus is not costly and I hope the description I have given of it is sufficiently clear to enable it to be easily understood and imitated.

ON THE DETERMINATION OF NITRATES IN POTABLE WATER.

BY AUGUSTUS H. GILL.
Received January 16, 1894.

PART I.

THE remark of Tiemann,¹ that the estimation of no other substance has so constantly occupied the attention of the analytical chemists of the last decade to the extent to which the determination of nitric acid has engaged (literally "enchained") them, will, I think, be appreciated by all those who have worked upon the subject. Perhaps no determination requires more care, or occasions more trouble in its execution, or is more unsatisfactory when finished, than the one in question.

There are two general modes of procedure:

- a. The direct estimation, and
- b. The reduction to ammonia.

a. DIRECT ESTIMATION.

The direct processes which have been found to give the best results are those of Schulz-Tiemann,² Schloesing-Reichardt,³ Crum-Lunge,⁴ and Marx-Trommsdorf.⁵ These are only appli-

¹ Tiemann Gaertner "Wasseranalyse" 3rd. Ed'n, p. 168.

² *Ber. d. chem. Ges.*, 6, 1041.

³ *Ztschr. anal. Chem.*, 9, 24.

⁴ *Phil. Mag.*, (3), 30, 426.

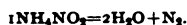
⁵ *Ztschr. anal. Chem.*, 9, 171.

cable where relatively large amounts of nitrate are to be estimated, over 0.6 parts of nitrogen as nitrate per 100,000, and even with this quantity two or three hundred cc. of the water must be evaporated for use. This concentration is objectionable as it offers an opportunity for the oxidation of nitrites and their decomposition with loss of nitrogen,¹ and also for the oxidation of organic matter, and where many determinations are to be made it is very troublesome.

There is too, a decided advantage in estimating the nitrogen contents *immediately upon receipt of the sample, and if possible, upon the water as received.* This has been pointed out by Tidy² in reference to the carbon contents of a water, and applies with still greater force to the nitrogen which is more susceptible to change.

Another direct method is the phenolsulphonic acid process; it originated with Sprengel³ and apparently fell into disuse until it was again brought to notice by Grandval and Lajoux.⁴ Since then articles upon it have appeared by Fox,⁵ Johnson,⁶ Lindo,⁷ Smith,⁸ Bartram,⁹ and Hazen and Clark.¹⁰

The two latter have criticised the process severely, and it seems to me unfairly, and it was with the idea of seeing how far



² *J. Chem. Soc.*, 35, 53 and 97.

³ *Pogg. Ann.*, 121, 188.

⁴ *Compt. rend.*, 101, 62.

⁵ *Tech. Quarterly*, 1, 1.

⁶ *Chem. News*, 61, 15.

⁷ *Chem. News*, 58, 1, 15, 28.

⁸ *Analyst*, 10, 197.

⁹ Bartram, *Jour. Frank. Inst.*, March 17, 1891, has published an article entitled "A Source of Error in the Determination of nitrates in Water by the Phenolsulphonic Acid Process," in which he says it was found that the phenolsulphonic acid undergoes a change after preparation. As ordinarily prepared, it may possibly undergo a change to the para acid; any difficulty is now obviated by the use of the pure disulphonic acid. I think the method has been submitted to an unusually severe test, 0.5 parts of nitrogen to 20 parts chlorine being very rarely met with in water analysis. It is unadvisable to estimate nitrates higher than 0.1 as it cannot be done with accuracy. Possibly the nitrate solution itself may have varied. I have solutions which contained 1 part of nitrogen as nitrates per 100,000 and which in the course of seventy-two hours showed but 0.04 part, and in ninety-six hours none whatever. Another containing 4.5 parts, showed at the end of six days but 0.25 part.

¹⁰ *J. Anal. Appl. Chem.*, 5, 1.

their critique could be supported by experiment that this investigation was undertaken.

The process consists in evaporating the water,—usually ten cc.,—to dryness in a porcelain dish, treating the residue with phenolsulphonic acid, diluting with water and neutralizing with ammonia. In presence of nitrates, ammonium picrate is formed, the color of which is matched by standard solutions of potassium nitrate which have been treated in like manner.

One of the principal objections is the formation of the three nitrophenols "the principal products being the ortho and para *mono* nitrophenol." This cannot be the case: according to Richter,¹ in the presence of a large excess of strong sulphuric acid—as we have here—the nitration goes farther, forming the di and tri-substituted compound. Granted, however, that the different amounts of these compounds were formed, it would be exceedingly anomalous to have under exactly the same conditions, at one time a large quantity of dinitrophenol formed, and at another time a large quantity of the trinitro body. Furthermore, the readings given in their comparative table of the various nitrophenols are probably incorrect; it has been found impossible to read colors as deep as 1.2 parts nitrogen per 100,000 in an eight inch tube more closely than twenty-five per cent.

The suggestion of one of them,² of making up standards in eight inch tubes and allowing them to stand "for months," has been found to be of no advantage, as a very decided deterioration does take place. The other suggestion, of making up standards by dilution of a solution obtained by treating a large quantity of potassium nitrate, is open to the objection that the colors produced are not the same as those from making up each one in a dish separately. In this connection I would remark that the same holds true of the colors produced by the Nessler reagent; for example, ten cc. of standard ammonium chloride is made up to 100 cc. and the reagent added. The colors produced by diluting one cc., five cc., or ten cc. of this (colored) solution to fifty each are not the same as those obtained by diluting 0.2

¹ *Lehrbuch d. Org. Chemie.*, 5th Ed'n., 572.

² Hazen, Report Mass. State Board of Health. "Purification of Sewage and Water," 1890, 712.

cc., one cc., or two cc. of the standard ammonium chloride solution each to fifty cc. and adding the Nessler reagent, but in every case darker.

The process is dismissed with the remark: "We have not been successful in so controlling the reaction as to get a constant product." The chief agents in the action of nitric acid upon any compound are heat and concentration. If, therefore, the dishes containing the residues are always at the same temperature,—which they must be, being at the temperature of the room—and the acid used of the same composition, it is difficult to see how the results could fail to agree in every case, and direct experiment proves this to be so, equal quantities of pure nitrate solutions agreeing exactly.

The investigation was conducted with reference to the following points.

I. ACIDS.

- a. Various acids.
- b. Method of treatment.
- c. Quantity of acid used.

II. EVAPORATION.

- d. Effect of sodium carbonate.
- e. Temperature at which it is carried on.
- f. Quantity evaporated.
- g. Effect of chlorine.

III. COMPARISON WITH STANDARDS.

The preparation of the phenolsulphonic acid is a matter of first importance, and for which, strange to say, no one has ever given definite directions. Kekulé¹ found when phenol and sulphuric acid were mixed, according to the temperature, varying amounts of ortho and para phenol monosulphonic acids were formed. As these could not fail to influence the action upon the dry-water residue, an acid of perfectly definite composition,—the pure disulphonic acid $C_6H_4OH(SO_3H)_2$, probably $OH : SO_3H : H : SO_3H = 1 : 2 : 4$, which with nitric acid gives *picric acid even in the cold*,²—has been mostly used in these experiments.

This is prepared as follows: three grams of phenol of good quality and thirty-seven grams of pure sulphuric acid sp. gr.

¹ *Ztschr. für Chemie*, 10, 199.

² Kekulé Lehrbuch III, 236.

1.84 (Kahlbaum's synthetic phenol and Baker and Adamson's "Strictly Pure" sulphuric acid were usually employed) are mixed in a flask and heated for six hours *in, not upon*, a water-bath to 100°.

To determine the number of sulphonic groups, a portion of this mixture was neutralized with barium carbonate, lixiviated with water, filtered, the filtrate evaporated and the barium salt recrystallized, giving handsome orthorhombic prisms. A determination of barium in this gave 35.16 per cent., the theory requiring 35.22 per cent. A determination of water of crystallization gave 15.66 per cent., theory, 15.62 per cent. H_2O . The acid as thus prepared may crystallize out upon standing, it being rather insoluble in the strong sulphuric acid, in which it forms supersaturated solutions. It may be brought into solution by reheating a short time, or by dilution with a small quantity of water, the undiluted acid has always been used.

The experiments were performed as follows: Two solutions were employed, one containing in one cc., 0.1000 part of nitrogen per 100,000 as potassium nitrate; the other in addition to this seven parts chlorine as sodium chloride per 100,000. Of these, portions of one cc. each were measured out and diluted to five and ten cc. with distilled water and evaporated in porcelain dishes.¹

The 2½ inch evaporator containing the water residue was moistened with ten drops—0.7 cc.—of the phenolsulphonic acid, and by rubbing with a short glass rod every part of the residue covered with it; seven cc. of water are now added,—measured in later experiments by a Vanier² overflow pipette,—the solution stirred and three cc. ammonium hydrate, measured in like manner, added, the solution again stirred to insure uniformity, and the rods removed. In many cases the colors could be compared directly in the dishes, but in case of doubt the comparison took place in tubes about 1½ inches deep and ⅝ inch in diameter.

¹ A convenient way of marking these dishes is to remove a small patch of the glaze upon the outside of the dish by glass etching ink, leaving a rough surface for the lead pencil.

² *J. Anal. Chem.*, 2, 145.

Each determination is the average of at least two closely agreeing determinations.

All results are stated in parts per 100,000.

I. ACIDS.

(a) VARIOUS ACIDS.

Equal parts of phenol and } The colors obtained were brown and an ac-
sulphuric acids. } curate matching was impossible.

Unknown mixture of ortho and } The colors obtained were fairly good,
para sulphonic acids from five } but in some cases were reddish
per cent. solution of phenol. } tinted.

Pure ortho phenol mono- } This gave a precipitate with the ammonia and
sulphonic acid.¹ } the colors were all bluish-green tinted.

Pure disulphonic acid, } The colors obtained were a pure yellow and
7½ per cent. solution. } did not change upon standing. This, there-
fore, gives the best results.

(b) METHOD OF TREATMENT.

At 100°.—Sprengel² states that the residue should be nearly at 100° when treated. Experiments performed by treating the residues upon the steam-bath with the cold acid and also with the acid at 100° gave no better results than those obtained in the ordinary way.

At 0°.—Treatment of the chilled residues upon ice with ice-cold acid gave decidedly lower results than those obtained in the usual manner, the nitration probably not going as far.

Addition of substances.—The addition of phenol or phenolsulphonic acid to the water before evaporation is of no advantage whatever.

(c) QUANTITY OF ACID USED.

If chlorine be absent or in small quantity, the amount of acid used makes very little difference. Enough should be used to cover the residue readily, usually ten drops=0.7 cc. is sufficient. For example, with equal quantities of the same nitrate solution which should have given a reading of 0.1000, the following results were obtained:

¹ Prepared by the cold evaporation in vacuo of the officinal solution of Merck's "Aseptol" and subsequent solution in sulphuric acid.

² *Pogg. Ann.*, 121, 188.

TABLE I.

Showing the effect of the quantity of acid used.

| Without Chlorine. | | With Chlorine, seven parts. | |
|-------------------|----------|-----------------------------|----------|
| 10 drops acid. | 6 drops. | 10 drops acid. | 6 drops. |
| 0.0925 | 0.9000 | 0.0750 | 0.0700. |

It is evident then that the use of too little acid causes the loss of nitric acid.

II. EVAPORATION.

It is well known that certain salts in solution undergo decomposition when boiled. Fittig¹ found this to be true of ammonium chloride, Debbits² of several acetates with loss of acetic acid, and with the nitrate, sulphate, acetate and oxalate of ammonium with loss of the respective acids. Leeds³ and Fox⁴ have shown that nitrates are volatile at 100° and even lower temperatures.

In order to ascertain what the influence of the evaporation really was, the following experiment was tried:

An intimate mixture of dry finely powdered potassium sulphate and nitrate was made by grinding them together in an agate mortar for several hours. Sixteen portions of 100 milligrams each were accurately weighed out, each containing about 0.072 milligram of potassium nitrate. Twelve portions were dissolved each in ten cc. of water, four of these evaporated at 100°, four at 65°, and the remaining four at 20° over sulphuric acid.

TABLE II.

Showing loss of nitrate by evaporation at various temperatures.

| | Dry. | 20°. | 65°. | 100°. |
|--------------|--------|--------|--------|--------|
| I | 0.1000 | 0.0890 | 0.0900 | . . . |
| II | 0.1050 | 0.1000 | 0.1080 | 0.1160 |

The readings varied among themselves by 0.0200 and hence were averaged.

To obviate this variation, sixteen portions of one cc. each of a nitrate solution were measured out, nine cc. of water added and all allowed to evaporate over sulphuric acid at a temperature of 20°. Ten cc. of water were added to each one of twelve of

¹ *Ann. Chem. Pharm.*, 128, 189.

² *Ber. d. chem. Ges.*, 5, 820.

³ *Am. J. Sci.*, (3) 7, 197.

⁴ *Tech. Quarterly*, 1, 1.

these and four evaporated at 20°, four at 65°, and four at 100°; this gave a series in which exactly the same amount of nitrate in every case was spread uniformly over the dishes and had been subjected to these various temperatures.

TABLE III.

Showing loss of nitrate by evaporation at various temperatures.

| Dry | 20° | 65° | 100°. |
|--------|--------|--------|--------|
| 0.1000 | 0.0990 | 0.0965 | 0.0990 |

These results indicate that there is a loss of about one per cent. when the water is allowed to evaporate at ordinary temperatures over sulphuric acid, or in a steam-bath where it evaporates rapidly and is *immediately* removed; at 65° where the evaporation is slower, and the time of exposure to heat consequently lengthened, the loss is greater, in this case about three and a half per cent.

(b) EFFECT OF SODIUM CARBONATE.

With a view of fixing the nitric acid and thus diminishing the loss by evaporation, it has been suggested that carbonate of sodium be added to the water before evaporation; as carbon dioxide is given off upon treatment with acid, it is possible that this carries off with it a slight quantity of nitric acid. Ten portions each of nitrate solution, the reading of which should have been 0.1000, were evaporated, the average reading was 0.0970, with the addition of soda 0.0973. Ten portions each of the same solution, containing in addition seven parts chlorine per 100,000, when similarly treated gave 0.0821, with the addition of soda 0.0812.

The avidity of acetic acid being much less than that of nitric acid, added to the fact that it was non-volatile at the temperatures employed, led to the suggestion that some of its salts be employed as a substitute for the sodium carbonate. Sodium acetate when added to the water, gave rather lower results than those obtained when it was not used.

(e) TEMPERATURE AT WHICH EVAPORATION IS CARRIED ON.

The accompanying table shows clearly the effect of temperature upon the determination.

The solutions should have all read 0.1000 part nitrogen as

potassium nitrate per 100,000, they were all treated with carbonate of sodium and each figure represents the mean of two closely agreeing determinations.

TABLE IV.

Effect of temperature.

Pure niter solution.

| Temp. | Quantity evaporated. | | |
|-------|----------------------|--------|--------|
| | 1 cc. | 5 cc. | 10 cc. |
| 100°. | 0.0925 | 0.0920 | 0.0920 |
| 65°. | 0.0890 | 0.0890 | 0.0880 |
| 20°. | 0.1050 | 0.0980 | 0.1000 |

Niter solution with 7.0 parts chlorine.

| Temp. | Quantity evaporated. | | |
|-------|----------------------|--------|--------|
| | 1 cc. | 5 cc. | 10 cc. |
| 100°. | 0.0680 | 0.0700 | 0.0600 |
| 65°. | 0.0650 | 0.0650 | 0.0680 |
| 20°. | 0.0935 | 0.0920 | 0.0700 |

It is evident that there is a decided loss of nitrate when evaporation takes place at 65° (the temperature which water assumes in a porcelain dish when upon the top of a water-bath) over that lost at 100° and here even over that lost at 20°. With chlorine this is even more perceptible; the reason for the increased loss at 65° is probably, as already stated, that the time of exposure at this temperature is longer.

It is important, however, that the dishes be removed as soon as dry, as the subsequent exposure causes loss of nitrate.

TABLE V.

Effect of heat upon the dry residue.

Water contained 0.1000 part N as N_2O_5 , 7.0 part Cl.

| | Quantity evaporated. | | |
|---------------------------------------|----------------------|--------|--------|
| | 1 cc. | 5 cc. | 10 cc. |
| Removed at once | 0.0750 | 0.0710 | 0.0740 |
| Exposed half an hour at 65° | 0.0700 | 0.0625 | 0.0690 |

(f) QUANTITY OF SOLUTION EVAPORATED.

The quantity of solution evaporated seems to exercise but slight influence upon the results, although the smaller it is, the less the loss; this is evident from all three of the preceding tables.

(g) EFFECT OF CHLORINE.

The presence of large quantities of chlorides in the water does

unquestionably lower the results. If the process be conducted in the usual way, by the evaporation of ten cc. at 100° it shows in Table IV, a loss of from thirty to forty per cent. of nitrogen as nitrate. If a smaller quantity, five cc. or even one cc., be used, and the evaporation be carried on at 20° over sulphuric acid, this loss is reduced to six or seven per cent., and of this probably one half is due to unavoidable errors in matching the colors.

If the chlorine amounts to but 2.0 parts per 100,000, which is perhaps high in waters of doubtful character, it exercises practically no influence.

TABLE VI.

Effect of 2.0 parts of chlorine (as NaCl) per 100,000. Readings should be 0.1000.

| | 1 cc. | 10 cc. |
|-----------------|--------|--|
| 100° . | 0.0900 | 0.0900 (average of five determinations.) |
| 65° . | 0.0900 | 0.1000 |
| 20° . | 0.0975 | 0.1050 |

III. COMPARISON WITH STANDARDS.

The yellow color of the picrate solution when as high as 0.1000 is extremely hard to match accurately; the tints must be read off at once without any delay as the difficulty increases with the time spent in comparison. It is well after reading perhaps a dozen, to rest the eyes by looking intently at a piece of blue paper.

As a result of a long series of experiments upon three different people,—all experts in the comparison,—it was found that the error of reading colors up to 0.0500 part N as N_2O_3 was 0.0020 or 0.0030; up to 0.1000 part N as N_2O_3 was 0.0050.

No advantage was gained by the use of colored glasses or, when the colorimeters were used, of colored papers underneath them.

The process does not, as stated by Grandval and Lajoux,¹ and also in Graham-Otto,² estimate the nitrogen present as nitrates; this is clearly impossible, as the action of nitrous acid upon phenolsulphonic acid results in the formation of nitrosophenol

¹ *Compt. rend.*, 101, 62.

² *Lehrbuch d. anorgan. Chem.*, 2, Part 1, 200.

$\text{C}_6\text{H}_5\text{NO}_2$ which is colorless in dilute solution. This view was supported by an experiment with pure sodium nitrite prepared from pure silver nitrite, in which no color whatever was obtained upon treatment with the phenolsulphonic acid.

The results of this paper may be summarized as follows:

The most satisfactory manner of execution is,—in the case of a water high in nitrates,—to use that quantity which will give a reading of about 0.0700 when one or two cc. are employed; in the case of ground water ten cc. of a portion which has been decolorized by the use of alumina in the cold, is evaporated upon the water-bath, the dish being placed in the steam and removed *as soon as dry*, or better, when a drop is still remaining. In case the chlorine be high, which often accompanies high nitrates, this evaporation had best take place in vacuo over sulphuric acid, and the chlorine, if it exceeds 7.0 parts per 100,000, removed by silver sulphate which has been proved to be free from nitrate.¹

In case one or two cc. of the water is used the 0.7 cc. of acid used is sufficient to cover the residue completely.

The error of reading up to 0.0500 is 0.0020 or 0.0030, four to six per cent. Up to 0.1000 is 0.0040 or 0.0050, four to five per cent., but the process as here described is more trustworthy, delicate and accurate than any process yet published.

For easy comparison 0.720 gram KNO_3 can be dissolved in one liter of water, ten cc. of this allowed to evaporate in vacuo, treated with acid, made up to a liter and portions as wanted made alkaline with ammonia, of this ten cc.=0.1000 part nitrogen as potassium nitrate per 100,000.

Acknowledgment.—The writer would hereby acknowledge his indebtedness to Prof. Drown and Mrs. E. H. Richards, chemists to the Massachusetts State Board of Health, for hints and suggestions, and to Miss Isabel F. Hyams and Mr. H. C. Tuttle, also of the Board of Health staff, for valuable assistance in making many of the readings involved in the preceding work.

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¹Samples from E. Merck, marked "C. P." contained enough nitrate to vitiate all results.

EXPERIMENTS ON THE ANALYSIS OF PIG COPPER, BRASSES AND BRONZES.

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Received January 17, 1894.

IN a recent number of this JOURNAL (January, 1894) a preliminary note was given on a method for systematic examination of pig copper and high copper percentage alloys. It is proposed in this paper to present some of the experiments involved in the work of which the note was a résumé. The results are familiar to those working in copper analysis, but on taking up the subject I was not able to find in the literature accessible to me quantitative data of many current statements. It is known for instance, that in determining tin in copper alloys by solution in nitric acid that phosphorus and arsenic remain in their oxidized forms with the metastannic acid but it was sought to ascertain whether the reaction was quantitatively exact or whether phosphorus and arsenic were still to be looked for in the filtrate from the residue.

Taking up tin the question was as to how that metal alloyed with copper reacted during analysis. The usual method of determining tin in such alloys is by solution in nitric acid, evaporating off excess of acid, diluting and when the precipitate has settled, filtering. The points to be taken into consideration are: 1. Whether or not the metastannic acid formed is soluble in nitric acid. Experiment answers this negatively. 2. Whether or not the metastannic acid is soluble in ammonium hydroxide, ammonium nitrate, or both. Experiment answers this also negatively. 3. The state of purity in which the residue is obtained. It is a matter of experience that in nitric acid solution, especially when evaporated to a point where basic salts are liable to form, the stannic oxide is found to be more or less contaminated with such salts of copper, manganese, and iron. These impurities adhere most tenaciously and washing with dilute nitric acid will not remove them completely. The reaction of tin phosphate and arseniate holds quite rigidly. The attack on tin by nitric acid is a solution and conversion into

an oxidized form and in this reaction if phosphoric or arsenic acids be present the stannic phosphate or arseniate is formed which, like the bismuth salts, is insoluble in nitric acid of five per cent. or less strength. The importance of this reaction in copper analysis is very great. With the exception of certain special alloys the tin present will generally exceed the quantity necessary to hold the arsenic and phosphorus in an insoluble form and the phosphate and arseniate of tin are not readily decomposed by simple digestion with alkali sulphide (S_n) but require fusion.

The following experimental results were obtained. Expressed in grams or fractions thereof. The term "metastannic acid" is used to indicate the residue obtained on dissolving tin in nitric acid, but such residue also contains stannic acid.

I. Solubility of the metastannic acid or residue obtained on dissolving pure tin in nitric acid. Excess of acid removed by evaporation to pasty condition. Dilution forty cc. Filtered after twelve hours.

| | | | | | | |
|-------------------|------|------|------|------|------|------|
| Tin taken | 1368 | 1544 | 1610 | 1744 | 1623 | 1674 |
| Tin found | 1365 | 1557 | 1620 | 1745 | 1630 | 1683 |

II. Solubility of the metastannic acid or residue obtained. Dissolving the tin in excess of nitric acid. Present 6.92 free nitric acid. Dilution 150 cc. Filtered after twelve hours.

| | | | | | |
|---------------------|------|------|------|------|------|
| Tin taken | 1812 | 1734 | 1795 | 1808 | 1746 |
| Tin found | 1812 | 1738 | 1792 | 1800 | 1732 |

III. Solubility of the metastannic acid or residue obtained. Dissolving in nitric acid. Evaporating to paste. Diluting to forty cc. and digesting twelve hours with five grams ammonium nitrate.

| | | | | | | |
|-------------------|------|------|------|------|------|------|
| Tin taken | 1963 | 1822 | 1763 | 0600 | 1814 | 1280 |
| Tin found | 1965 | 1842 | 1784 | 0602 | 1839 | 1301 |

IV. Solubility of the metastannic acid or residue obtained. Conditions as in III. Digesting twelve hours with 6.52 NH_3 .

| | | | | | | |
|-------------------|------|------|------|------|------|------|
| Tin taken | 1653 | 1472 | 1785 | 1530 | 1671 | 1242 |
| Tin found | 1679 | 1498 | 1808 | 1563 | 1690 | 1260 |

V. Solubility of metastannic acid or residue obtained. Conditions as in III and IV. Digesting twelve hours with five grams $NH_4NO_3 + 6.52 NH_3$.

| | | | | | | |
|---------------------|------|------|------|------|------|------|
| Tin taken | 1495 | 1527 | 1357 | 1731 | 1567 | 1511 |
| Tin found | 1534 | 1567 | 1408 | 1784 | 1606 | 1546 |

VI. Precipitation of tin by NH_4HO . Five grams of copper present 6.92 free HNO_3 . Ammonia added at once to re-solution of the copper salt. Filtered after twelve hours. All contaminated with copper oxide. Washed with dilute nitric acid.

| | | | | | |
|---------------------|------|------|------|------|------|
| Tin taken | 1986 | 1770 | 1779 | 1928 | 1977 |
| Tin found | 2095 | 1907 | 1866 | 1998 | 1958 |

VII. P_2O_5 remaining with metastannic acid. Excess of tin present. Phosphor-tin treated with nitric acid. Evaporated to paste. Dilution forty cc. Present 0.0631 phosphorus in one gram.

| | | | | | |
|----------------------------|--------|-------|-------|--------|-------|
| Phosphor-tin taken . . . | 3150 | 2580 | 2763 | 2400 | 0990 |
| P in filtrate | 0003 | trace | trace | 0004 | trace |
| Per cent. P in residue . . | 99.905 | | | 99.983 | |

VIII. P_2O_5 remaining with metastannic acid. Excess of phosphorus present. Conditions as in VII. Present 0.0250 phosphorus.

| | | | | | |
|-----------------------|------|------|------|------|------|
| Tin present | 0078 | 0076 | 0067 | 0077 | 0075 |
| P combined | 0190 | 0146 | 0131 | 0151 | 0154 |

The ratio of SnO_2 : P_2O_5 is 1 : 4 (on averaging).

IX. As_2O_3 remaining with metastannic acid. Excess of tin present. The arsenic and tin treated with nitric acid. Conditions as in VII. Present 0.0067 arsenic.

| | | | | | |
|-----------------------------|------|------|------|------|------|
| Arsenic in filtrate | 0012 | 0009 | 0011 | 0012 | 0011 |
| Per cent. As in residue . . | 83.5 | 86.6 | 83.6 | 83.6 | 83.6 |

X. As_2O_3 remaining with metastannic acid. Excess of arsenic present. Conditions as in IX. Present 0.0134 arsenic. In filtrate.

| | | | | | |
|--------------------------|------|-------|------|-------|-------|
| Arsenic | 0129 | 0121 | 0129 | 0107 | 0113 |
| Per cent. loss | 3.73 | 11.19 | 3.73 | 20.15 | 15.67 |

In both IX and X tin and arsenic were attacked by nitric acid in presence of each other. In IX there was a large excess of tin (0.1000 gram). In X there was 0.0095–0.0110 tin present. The operations were conducted in the same manner and repeated.

XI. Phosphate of tin with metastannic acid. Digested at 70° for five hours with excess Na_2S .

| | | | | | |
|-----------------------------|------|------|------|------|------|
| Phosphorus present | 0071 | 0046 | 0069 | 0061 | 0136 |
| P as unconv'd phosphate . . | 0024 | 0018 | 0041 | 0037 | 0114 |
| Per cent. unconverted . . . | 33.8 | 37.1 | 59.4 | 60.3 | 83.8 |

No. 5. (83.8) in solution in nitric acid was inadvertently carried to complete dryness.

XII. Arseniate of tin with metastannic acid. Digested at 70° for five hours with ammonium sulphide. Filtered from residue after twelve hours. Present 0.0067 arsenic.

| | | | | | |
|------------------------------|-------|-------|-------|-------|-------|
| As as unconv'd arseniate . . | 0051 | 0057 | 0055 | 0058 | 0057 |
| Per cent. unconverted . . . | 76.12 | 85.07 | 82.09 | 86.56 | 85.07 |

The residue, acids of tin, were converted by ignition in a porcelain crucible, to stannic oxide. The full heat of a Fletcher lamp was used. Phosphorus was precipitated by molybdic solution and weighed as $Mg_3P_2O_7$. Arsenic was weighed as $Mg_3As_2O_7$.

With antimony a number of similar experiments were carried out. The antimony was weighed as Sb_2O_3 and Sb_2S_3 .

XIII. Solubility of the residue obtained by dissolving pure antimony in dilute nitric acid (1-3) evaporated to pastiness. Dilution forty cc. Filtered after twelve hours.

| | | | | | |
|--------------------------|------|------|------|------|------|
| Antimony taken | 1004 | 1186 | 1198 | 1243 | 1120 |
| Antimony found | 0947 | 1151 | 1170 | 1232 | 1017 |

XIV. Residue as in XIII. Nitric acid solution containing 6.92 free nitric acid. Diluting 150 cc. Filtered after twelve hours.

| | | | | | |
|--------------------------|------|------|------|------|------|
| Antimony taken | 2214 | 2166 | 2244 | 2600 | 2277 |
| Antimony found | 2046 | 1829 | 2079 | 2537 | 2160 |

XV. Residue as in XIII. Digested twelve hours with 6.52 NH_3 . Dilution forty cc.

| | | | | | |
|--------------------------|------|------|------|------|------|
| Antimony taken | 1012 | 1000 | 1584 | 1278 | 1100 |
| Antimony found | 0982 | 0965 | 1551 | 1272 | 1038 |

XVI. P_2O_5 remaining with the oxides of antimony on solution of metallic antimony in nitric acid. Excess of antimony present. Evaporated to pastiness. Diluting forty cc. Present 0.0051 phosphorus.

| | | | | | |
|----------------------------|-------|-------|-------|-------|-------|
| Phosphorus in filtrate . . | 0020 | 0033 | 0018 | 0018 | 0015 |
| Per cent. P in residue . . | 60.78 | 25.29 | 64.70 | 64.70 | 70.59 |

Antimony is a most troublesome determination to make in copper analysis. If it can be separated and obtained in a precipitate of small bulk the solubility of the sulphide in alkali sulphide can be taken advantage of, but to apply this reaction in

the presence of ten to twenty grams of copper in the form of an easily oxidized sulphide is a difficult and tedious operation.

The object of the use of ammonia and barium hydrate is to effect for copper what is done in iron analysis for single determinations. In separating manganese or phosphorus in a steel, one of the objects is to retain the iron in solution, precipitating out the element which is present only in small quantities. The bulk of the copper being held in solution by the ammonia and precipitation being completed by barium hydrate the analysis of a pig copper is simplified by having a small precipitate to work upon. An excess of barium hydrate being used the separation of the crystalline barium carbonate probably has its effect in the filtration. If we have to make a systematic examination of a copper alloy, as in any case the residual tin oxide obtained by the nitric acid method would have to be purified, it is easier to do this work of purification and separation in such a way as to obtain quantitative results of the different minor constituents sought. If there is enough iron, tin, etc., to fix all the phosphorus and arsenic in an insoluble form the results are quantitative for these elements. To add ferric chloride to obtain such results may be of advantage, but iron is an important object of search in such examination and these two elements are not difficult to separate from the main bulk of copper by other methods. Only special alloys, such as phosphor-bronze or a manganese-copper alloy made with ferro-manganese contain notable quantities of phosphorus. Phosphorus is also sometimes present in aluminum brass, and a sample was found to contain 0.056 per cent. P to 0.22 Fe. Where phosphorus and arsenic are used as deoxidizers, only a very small quantity is to be found on analysis.

To properly precipitate iron, aluminum, or bismuth by ammonia it is necessary to avoid a large excess of the reagent, but in adding ammonia to re-solution of the copper salt an excess must be added and retained. Using test solutions for examination of the use of ammonia and barium hydrate the following results from sixty odd experiments were obtained:

| Element. | $\text{NH}_4\text{HO.}$ | $\text{NH}_4\text{HO} + \text{Ba}(\text{HO})_2.$ | Dilution. |
|--------------------|-------------------------|---|-----------|
| Phosphorus | not precipitated. | { not precipitated completely. | 100 cc. |
| Arsenic | " | precipitated. | 50 cc. |
| Nickel | " | not precipitated | " |
| Cobalt | " | " | " |
| Zinc | " | " | " |
| Cadmium | " | " | " |
| Silver | " | " | " |
| Bismuth | ppt. incomplete. | ppt. complete. | 150 cc. |
| Manganese | " | " | " |
| Antimony | " | { coloration by H_2S , trace in solution. | " |
| Tin | ppt. complete. | ppt. complete. | " |
| Lead | " | " | " |
| Iron | " (?) | " | " |

With arsenic in the ammoniacal solution of fifty cc. dilution the precipitation by $\text{Ba}(\text{HO})_2$ is complete, as barium ammonium arseniate (Douglas and Prescott, Qual. Anal.). In dilute solutions or on heating the precipitation becomes incomplete. Digestion with alkali sulphide (S_n) does not transpose this precipitate. Phosphorus is precipitated as barium phosphate. With a copper containing known quantities of the minor constituents the following results by the use of ammonia and barium hydrate were obtained: The original copper taken contained 0.03 per cent. Fe and 0.025 per cent. Pb as impurities. Allowance was made in calculating.

| Element. | Present. | Taken
10
grams
Cu | Taken
20
grams
Cu | Taken
30
grams
Cu | Taken
40
grams
Cu | Taken
50
grams
Cu |
|-----------------------|----------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Arsenic | 0079 | 0053 | 0051 | 0081 | 0079 | 0073 |
| Tin | 0041 | 0048 | 0043 | 0043 | 0030 | 0040 |
| Antimony . . . | 0048 | 0051 | 0050 | 0042 | . . | 0045 |
| Lead | 0053 | 0052 | 0056 | 0056 | 0060 | 0057 |
| Bismuth . . . | 0028 | 0030 | 0030 | 0026 | 0029 | 0034 |
| Cadmium . . . | 0295 | 0309 | 0307 | 0291 | . . | 0221 |
| Phosphorus . . | 0032 | 0024 | 0037 | 0029 | 0021 | . . |
| Dilution in cc. . . . | | 300 | 400 | (800) | 800 | 800 |

The difficulty arising in the use of thirty, forty, or fifty grams of the pig copper came from the separation of the copper-ammonium salts. The dilution was 800 cc. It also takes the equivalent quantity of potassium cyanide to decolorize the filtrate. If

the solution is allowed to stand but thirty to sixty minutes the copper salt is much diminished in quantity and the precipitate appears to be all down. Ten grams and a dilution of 150 cc. works well. The copper-ammonium salts are readily soluble in water on warming, and if arsenic and phosphorus are in the form of iron or other insoluble salt they are not affected by such treatment. The above results were obtained: By dissolving in nitric acid, adding ammonium hydroxide to re-solution of the copper salt followed by addition of excess of barium hydroxide, such excess being quickly indicated by the formation of the crystalline barium carbonate. Allowed to stand 30 to 120 minutes and filtered. Filtrate decolorized by potassium cyanide and precipitated by hydrogen sulphide.

In the July (1893) number of this JOURNAL Mr. Jesse Jones applies a method for the determination of manganese in bronzes based on Ford's method in steel analysis. In the course of the method as described he removes copper by hydrogen sulphide, filters and obtains the manganese from the filtrate. His paper simply describes the course of analysis without entering into any details as to why it was found necessary to remove the copper. In making some analyses for Mr. F. Lynwood Garrison (*Jour. Frank. Inst.*, June to September, 1891), Hannay's reaction, the oxidation and precipitation of manganese as manganese dioxide in the nitric acid solution by potassium chlorate, was applied at once and without removing copper. It was the suggestion of the late Dr. F. A. Genth to try this method as conducted in the analysis of steel and subsequent examination of the filtrate gave negative results for manganese. I have repeated the experiments to find out whether or not removing copper is a source of error and the results given below were obtained on a manganese brass, dissolved in nitric acid and made up to 100 cc. Aliquot portions were then taken, the manganese precipitated by potassium chlorate and titrated in neutral solution by permanganate. The variation is within reasonable limit and shows, I think, that there is no objection to proceeding with a copper alloy in the manner as with steel and that the removal of copper is not essential to accuracy.

00659 00659 00655 00647 00655 00640

I wish to acknowledge the kindness of Prof. F. A. Genth to whose encouragement was largely due the idea of putting these data into form, and of Mr. F. Lynwood Garrison to whom I am indebted for a number of alloys from his collection.

CHEMICAL LABORATORY,
123 S. SEVENTH ST., PHILADELPHIA, PA.

INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

SUB-COMMITTEE ON METHODS.

BULLETIN No. 1.

ORGANIZATION AND WORK OF THE COMMITTEE.

AT the World's Congress of Chemists, in Chicago, last August, following the papers of Professor J. W. Langley, "On the Work of the Committee on International Standards for the Analysis of Iron and Steel," and of Dr. C. B. Dudley, "On the Need of Standard Methods for the Analysis of Iron and Steel, with Some Proposed Standard Methods," was a brief discussion, which resulted in the reference by that body of the whole subject of standard methods for the analysis of iron and steel, to the Committee on International Standards for the Analysis of Iron and Steel. That committee, it will be remembered, consists of seven chemists, in each of five different countries; namely, England, France, Germany, Sweden, and the United States. The American Committee was appointed jointly by the American Society of Civil Engineers, and the University of Michigan, with Professor J. W. Langley, Case School of Science, Cleveland, Ohio, as chairman. The other members of that Committee were W. P. Barba, Midvale Steel Works, Nicetown, Philadelphia, Pa., A. A. Blair, 406 Locust street, Philadelphia, Pa., Professor Regis Chauvenet, President State School of Mines, Golden, Colorado, Professor T. M. Drown, Mass. Inst. Technology, Boston, Mass., Dr. C. B. Dudley, Chemist Penn'a. R. R. Co., Altoona, Pa., and Porter W. Shimer, Easton, Pa.

Following the reference of the subject to this committee, it

was decided after consultation to appoint a sub-committee, to take up the question of standard methods. The sub-committee is constituted as follows: W. P. Barba, A. A. Blair, T. M. Drown, Porter W. Shimer and C. B. Dudley, Chairman.

The sub-committee held an organizing meeting at the office of A. A. Blair, 406 Locust street, Philadelphia, on December 13, all the members being present. The object of the meeting was to map out the work. It was agreed as follows:

First. That Mr. Blair should submit a form of circular to go to the iron and steel chemists of the country, asking for a brief outline of the methods which they prefer, and the reasons for all the important points of their methods.

Second. That the work of the committee should comprehend the recommendation of standard methods to be used as the basis of commercial transactions, and when any of these methods could not be used in steel works in daily practice, on account of time required, an alternative rapid method should be recommended, and its limitations defined.

Third. That the members of the committee should draw up each proposed standard method in writing, with some minuteness, and give the reason for each important point, these written drafts to be sent to the chairman, to be duplicated, and sent to every member of the committee. Later, the points agreed upon are to be edited by some one member of the committee.

Fourth. That only one element should be embraced in a method.

Fifth. That the first method to be taken up, should be phosphorus in steel.

Sixth. Mr. Barba offered to furnish to each member of the committee, a suitable quantity, not less than a pound or so, of borings of three (3) different kinds of steel; namely, one of from 0.01 to 0.02 phosphorus, carbon about 0.90, and silicon about 0.40; another with phosphorus not far from 0.06, carbon 0.50 to 0.60, silicon 0.25 to 0.30, and arsenic 0.15 per cent. The above two, to be crucible steel. Another sample of open hearth steel of carbon 0.90 to 1.05, phosphorus 0.02 to 0.04, manganese 0.30 to 0.40, silicon 0.20 to 0.25, sulphur 0.02 to 0.04 and copper anywhere below 0.10.

Seventh. Dr. Dudley offered to furnish to each member of the committee, a like amount of borings from a sample of Bessemer steel of from, 0.10 to 0.12 phosphorus, carbon about 0.50, manganese 0.80 to 1.00, silicon 0.02 to 0.05, sulphur 0.07 to 0.10 and copper from 0.07 to 0.10. These samples of steel to be used in deciding various questions that may come up in regard to proposed methods.

A very earnest feeling was manifested at the meeting of the sub-committee, and the outlook for some good work, is apparently very favorable.

APPROVED:

J. W. LANGLEY,

Chairman Com. on Int. Standard.

CHAS B. DUDLEY,

Chairman Sub-Committee.

NEW BOOKS.

A MANUAL OF PRACTICAL ASSAYING. BY H. van F. FURMAN.

The constantly increasing demands made on metallurgical chemists for rapid work makes the appearance of Mr. Furman's book very timely; for while there are numerous text-books on assaying, and complete treatises for the iron-works chemist, no work until this has so completely embodied the methods now in use by the chemists of the silver, lead, and copper smelters of the west, and it is for these especially that the book is written.

On this account it would seem more appropriate to have included technical analysis in the title, for while the term assaying may doubtless be properly used as meaning more than fire assaying, it can hardly be construed into covering the contents of this book, which contains methods not in common use, by the technical chemist at least, and which in actual practice would probably be looked up in more detailed and specialized works. It would, however, hardly be just to criticise the author for making his manual as complete as possible, providing good judgment is used in selecting the methods, which is the case in all but a very few instances.

Part I, which is introductory, and includes chapters giving useful details as to reagents, apparatus, blowpipe reactions, etc.,

contains a chapter on sampling worthy of special mention. This chapter gives a thorough description of both hand and mechanical sampling as applied to the crude material, and to the finished products of the smelter. When it is remembered that the value of all the subsequent work depends upon having a good sample to start with, it can easily be seen that a knowledge of this subject is of great importance. As those accustomed to smelter work know, inaccurate sampling, either real or supposed, is the source of constant disputes; and anyone not already familiar with the various methods can read this chapter with profit.

Part II describes the methods for the separate determination of all the elements which need be considered in a technical manual; including a very full description of the fire assay for gold, silver, and lead.

Of course in a limited space no review can be attempted of all the methods given in this part of the book; but in general it can be said, that while there are perhaps occasional details which could be advantageously modified, they are methods which have stood the test of actual use under the trying conditions of smelter laboratories, where rapidity is the first and accuracy the second essential.

Some of the methods given here, while in constant use in the west, have not received the attention they deserve at the hands of analytical chemists in general; most conspicuous of these are the methods of A. H. Low for zinc, of H. H. Alexander for lead, and of F. C. Knight for lead, when used with the skill coming from practice, and with a proper understanding of the conditions involved, these methods, while essentially rapid, give results of a high degree of accuracy; they have a place indeed in the first rank of volumetric determinations.

The student of technical analysis can safely accept the methods given in Part II as carefully selected and reliable, and rendered additionally valuable by the liberal use of foot notes in referring to the original sources of information.

Part III is devoted to the description of special assays and analyses. The most important chapters here, of course, are those dealing with subjects which come up with more or less con-

stancy in smelter laboratories and assay offices; such as the assaying of the different kinds of bullion and mattes, and the analysis of slags, and these the author has treated very satisfactorily. In addition, among somewhat miscellaneous matter, are chapters on the analysis of gases, water, phosphates, etc., which in the absence of the standard text-books on these subjects will furnish a guide for doing such work, although the practice of trying to do chemical work without the proper fundamental knowledge cannot be too strongly deprecated.

Part IV, the last, includes chapters on the writing of chemical equations and stoichiometry, which are good in themselves, but of doubtful usefulness in a book of this kind, unless, perhaps, they are considered chiefly as preparing the way for the final chapter on the calculation of lead blast-furnace charges; a subject of much importance, and one which the author, from his own experience, is well fitted to treat.

A copious and well selected set of tables concludes the volume.

In his expressed object to "fill * * the wants of technical chemists" the author has certainly succeeded quite well, perhaps even too well; for with a volume of condensed information at hand the race of "machine" chemists, with which the west is already overstocked, will probably be increased. For this evil some of the western technical schools are primarily to blame. So long as they see fit to give a student a certificate of competency as a chemist or assayer when his stock of knowledge consists of an assortment—well selected it is true—of rule-of-thumb methods, just so long will the demand for this kind of education exist; and Mr. Furman, I fear, has unintentionally made it easier to get. While his book will be most useful to the well-trained analyst who can use the methods with discrimination, it can also be made to answer the purpose of the mechanical chemist as well.

L. G. BAKINS.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

NEW YORK SECTION.

Peter T. Austen, Presiding Officer.

Morris Loeb, Secretary.

PAPERS READ.

AUTOMATIC ZERO BURETTE.¹

BY EDWARD R. SQUIBB, M. D.

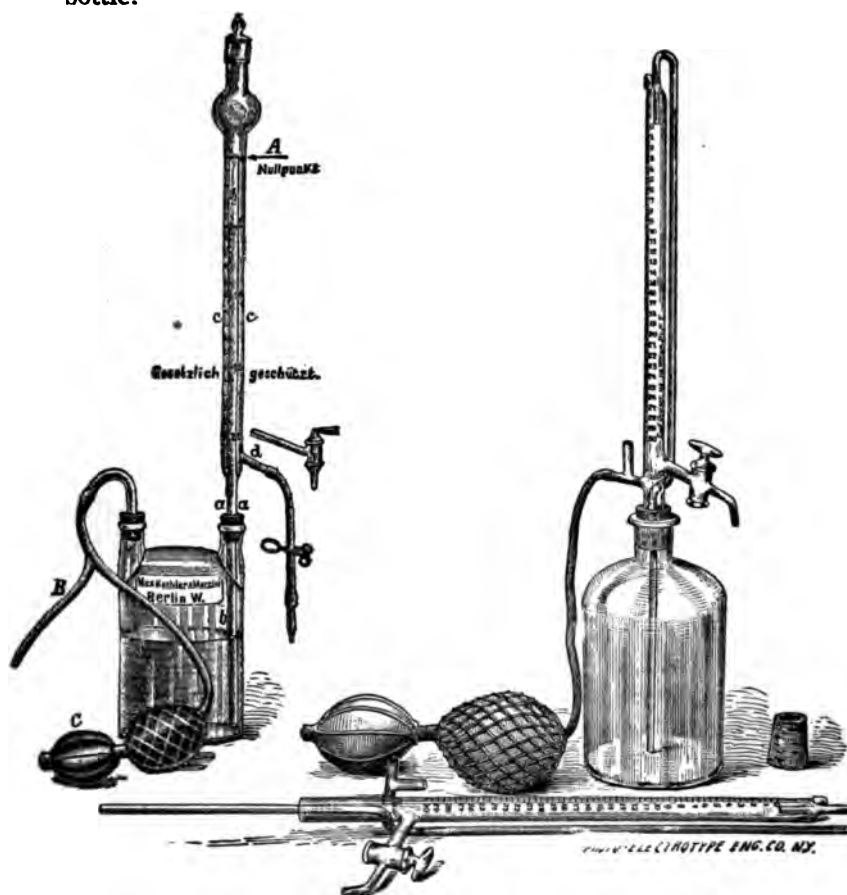
IN many manufactories and laboratories two or more volumetric solutions are in frequent use, and for such it is convenient to have a burette that can be rapidly used, and be carried about from place to place. This is practicable with the ordinary burette and stand. But then the bottle of volumetric solution has also to be carried about and much time is required in filling and adjusting to the Zero mark.

In the *Berichte der deutschen chemischen Gesellschaft* for October 24, 1892, No. 15, page 3010, Stanislaus Krawczynski has a description and cut of a new form of burette with an arrangement for automatic or mechanical filling to the zero point. The cut of this apparatus is reproduced here in the left-hand group of the first illustration plate in order that the inventor may have due credit for the physical principles of which he has availed himself.

On having a couple of these made for trial the writer observed that solutions of different physical properties gave different levels in overflowing through the central tube and were not fairly constant to the zero mark. Messrs. Eimer and Amend, of New York, had one made in which the internal tube was turned over upon itself for about one cm. at the upper end and this gave a

¹ Read December 8, 1893.

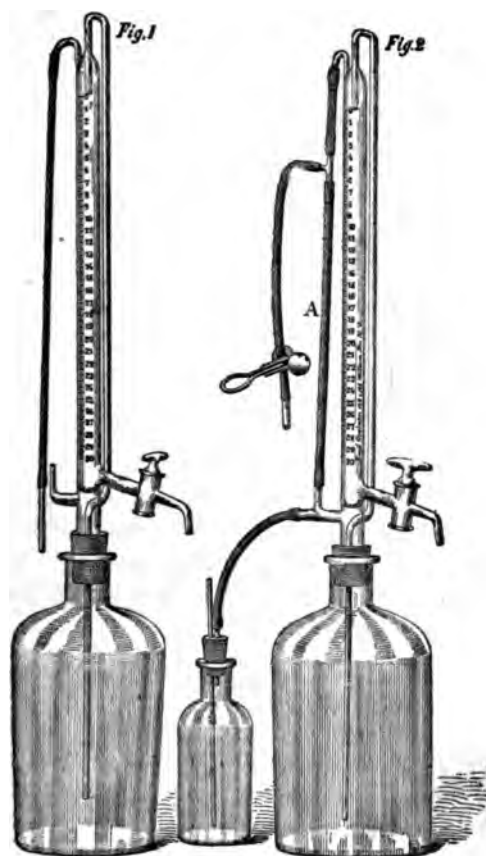
more uniform level with different solutions; and they substituted an ordinary Erlenmeyer flask of liter size for the two necked bottle.



But it was found impracticable to get the internal tube quite straight, and to have it exactly in the center of the outer graduated tube throughout its length, and the least variation in this condition gave a distorted meniscus. Then again the distortions were not uniform nor constant, but varied with the relations between the inner and outer tubes so as to disturb the values of the readings in different parts of the burette.

To overcome these disadvantages this writer simply put the filling tube from the bottle on the outside of the burette in the way shown in the right-hand group of the illustration. By this arrangement the excess of liquid blown over by the rubber pressure bulbs is siphoned off to the zero point with a fair degree of accuracy and uniformity after the finger is removed from the open end of the **I** tube on the left.

After a little experience with this modification it was easy to reach another that had still greater advantages over the last. In this the expensive and cumbersome rubber pressure bulbs are



dispensed with, and the burette is filled by mouth-suction, just as an ordinary pipette is filled. The apparatus shown by Fig. 1, of the second cut shows this design in its simplest form. Here the suction is applied at the top of the burette, the filling liquid rising from the bottle through the outside tube until the zero mark is passed. Then on stopping the suction the excess of solution is siphoned off to the zero mark and flows back into the bottle. If the apparatus is to be set aside for any considerable length of time it may be closed against the external

air by removing the glass mouth-piece from the suction tube.

and slipping the end of the rubber tubing over the turned up end of the glass tube by which air is admitted to the bottle to replace the solution drawn up the filling tube. But this is hardly necessary in any ordinary usage.

In many cases, however, it is necessary to exclude the carbon dioxide and other impurities of the laboratory air from volumetric solutions, and to prevent concentration of the solutions by evaporation of their water. These conditions are met in the modification shown in Fig. 2, of the second cut. Here a small wash-bottle is added, through which all the air admitted to the apparatus, either above or below, must pass, and be washed in passing. This bottle may be supplied with baryta water or lime water when it will serve to saturate the air through it with moisture, and free it from ordinary gases and vapors. In using this apparatus a pinch-cock is necessary on the rubber suction tube near the mouth-piece, by which the mouth-piece is conveniently handled, and during the suction this pinch-cock is opened and the rubber tube below is pinched at A by the thumb and finger of the left hand. This apparatus is constantly sealed from the external air, and is safe and accurate for any length of time, and is always in readiness for use, care being taken to well wash the end of the stop-cock, and to waste the solution that is outside of the cock whenever the apparatus has stood unused for even a few hours.

These burettes are very well made by Mr. Emil Greiner, of 146 William Street, near Fulton, New York City, who supplies them with or without the bottles as ordered. The only advantage in ordering the burette and bottle together is to have the internal tube of the right length to reach the bottom of the bottle.

A COMPRESSED AIR WASH-BOTTLE.¹

By W. C. FERGUSON.

THIS idea, not yet put in practical operation, was suggested by the difficulty attending the washing of such precipitates as hydrate of alumina, the complete removal of very small amounts of finely divided material from the sides of the contain-

¹ Read December 8, 1893.

ing vessels, such as gold in commercial copper, or of such precipitates as adhere with persistency, when the ordinary wash-bottle, with comparatively little pressure available, is used. It would also seem that such a device would facilitate the general washing of precipitates in a laboratory where sometimes a hundred or more filtrations are made in a single day.

The features of the idea are about as follows:

Compressed air would be the source of pressure, and in the laboratory of which the writer has charge it could be introduced very conveniently from the factory where it is used on a large scale. Mr. J. B. F. Herreshoff, the distinguished chemical engineer, suggested using a gasometer where no source outside of the laboratory was available.

The air pipe would be arranged with branches to the filter pumps, and also to any other part of the laboratory where filtrations would be carried on.

The wash-bottles would be large and stout, and the apparatus arranged so that they could be removed readily and refilled or replaced as required. The air pipes would be provided with stop-cocks, just above the bottle, for regulating the supply of air. Glass nozzles of about the same form and length as in the ordinary wash-bottle, but with orifices of different sizes would be used, so that a very fine jet or a large stream of water could be employed as desired.

Rubber tubing of suitable length and strength would connect the water-bottle and nozzle.

The jet would be further regulated by a pinch-cock just above the nozzle so as to be conveniently manipulated while washing.

The advantages of this device would seem to be a minimum amount of work in manipulation, and a more thorough washing due to increased pressure. Where a large amount of work is done each day and accurate, prompt reports are absolutely necessary, it is self-evident that all devices that reduce labor and in other ways increase efficiency, tend to raise the standard of results.

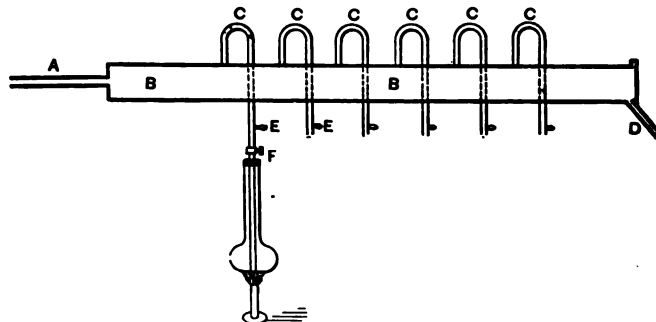
AN ARRANGEMENT FOR CONDUCTING A NUMBER OF LABORATORY DISTILLATIONS WITH STEAM, SIMULTANEOUSLY.¹

BY W. C. FERGUSON.

A is an ordinary $\frac{3}{8}$ inch iron steam pipe connected with the steam system in the factory and provided with a valve where it enters the laboratory. B is a brass pipe $1\frac{1}{2}$ inches in diameter, connected with A and inclining towards D, to facilitate the removal of condensed water.

The tubes C, are about $\frac{1}{8}$ inch in diameter and are provided with cocks at E.

When distillations are in operation the brass tubes C are connected with glass tubes by means of rubber tubing; the glass



tubes reach nearly to the bottom of the distilling flasks and are provided with ground glass stop-cocks at F. D carries off the condensed water from B.

The entire apparatus is suspended from the ceiling by stiff iron rods. The condensers are arranged at right angles to, and immediately underneath B. The table is provided with both cold water and waste pipes for the condensers.

B must be high enough to permit the use of Bunsen burners under the distilling flasks.

Before starting distillations, all of the cocks E, must be opened and steam turned on, to blow out condensed steam; they are then closed, the distilling flasks connected as described above

¹ Read December 8, 1893.

and the cocks E again opened, taking care to have the ground glass cocks F closed.

During distillation the steam is controlled by the stop-cocks F, and the operation is further regulated by the use of Bunsen burners under the distilling flasks. One person can easily attend to six or more distillations at one time.

Experience of more than a year has proved the utility of this arrangement, where many samples involving analysis by distillation, have been presented in a day.

A NEW MUFFLE FOR INCINERATION OF SUGAR.¹

BY H. SCHWEITZER AND E. LUNGWITZ.

THE incineration of sugar for the determination of ash is generally carried out in platinum dishes which are placed in a muffle of platinum (Scheibler) or of Russian sheet iron (F. G. Wiechmann) kept at a dull red heat. The platinum muffles to hold two dishes, weigh from sixty to seventy-five grams, and are very expensive apparatus. Moreover it happens very often that in a platinum muffle the last portions of carbon are oxidized with difficulty. Frequently a little higher temperature under the muffle of platinum which is such an extremely good conductor of heat, causes the ash to fuse and the melted salts, including unburnt carbon, form black blotches in the dish. On account of the insufficient draught in the platinum muffle it is then very difficult to accomplish perfect incineration. In such a case, as Tucker says in his manual of sugar analysis, the dish is allowed to cool, one or two drops of sulphuric acid added, and the dish heated cautiously at first to avoid spattering and finally brought to redness for fifteen minutes. Naturally such proceeding causes delay and does not contribute to the exactness of the determination.

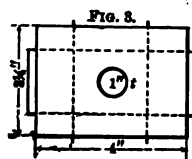
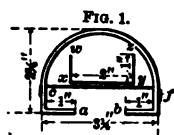
The muffles of iron are impracticable for quick commercial work because the incineration in them takes much longer time than in those of platinum.

These considerations prompted us to devise an apparatus, better fitted for the incineration of sugar than the muffles mentioned above.

¹ Read December 8, 1893.

The accompanying cuts show how we solved this problem.

A French clay muffle is cut open at the bottom; (see Fig. 1, *a, b*) through the walls of the muffle at both ends holes are bored (Fig. 2, *c, d*) through which platinum wires are fastened



in the manner shown in Fig. 1, *c, f*. These wires serve as support for the bent platinum sheet, (Fig. 1, *w, x, y, z*) on which the dishes containing the sugar are placed. In the center of the top of the muffle a round hole is cut out, (Fig. 3, *t*). The bent sheet *w, x, y, z*, can also be made of Russian sheet iron. The muffle is placed on a tripod and heated as usual.

This construction produces a good draught in the muffle and allows the use of the largest flame of the so-called "Acme" burner which accelerates the incineration very considerably. Whereas the complete incineration under normal conditions in a platinum muffle lasts from about forty to forty-five minutes, it lasts only twenty-five to thirty minutes in our platinum clay muffle and about forty-five minutes in our platinum iron muffle. The short time in which our platinum clay muffle works, naturally reduces the expense for gas. For about one year we have had both kinds of clay muffles in constant use and always obtain light and flaky ash and never a fused ash.

We feel assured that these new muffles, saving time and money, will be welcome additions to the outfit of every sugar laboratory.

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A FEW REMARKS ABOUT BASIC SULPHATE OF ALUMINA.¹

BY W. C. FERGUSON.

MANY samples of commercial sulphate of alumina contain more or less of an excess of alumina over that required to form the normal sulphate ($\text{Al}_2(\text{SO}_4)_3$), the amount varying from a trace to $2\frac{1}{2}$ per cent. and occasionally even more.

The following composition is of frequent occurrence:

Total soluble alumina = 17.00 per cent.; soluble alumina calculated from sulphuric anhydride (SO_3) to form $\text{Al}_2(\text{SO}_4)_3$ = 15.2 per cent., leaving 1.8 per cent. of alumina in excess of that required to form the normal sulphate.

It is concerning the probable chemical constitution of this alumina in excess of that required to form the normal sulphate, together with its behavior towards resin soap in the manufacture of paper, that this brief article is written.

As is well known, in sizing paper sulphate of alumina is made to react on resin soap (made by saturating soda ash with resin), thus precipitating an insoluble alumina soap, a resinate of alumina in the fiber of the paper.

In many paper works the per cent. of normal sulphate $\text{Al}_2(\text{SO}_4)_3$, determines the strength of the material bought and, other things being favorable, that is preferred which contains the highest per cent. of $\text{Al}_2(\text{SO}_4)_3$.

A number of reports from paper mills are about as follows:

$$\begin{array}{l} \left\{ \begin{array}{l} \text{Combined } \text{Al}_2\text{O}_3 = 15.20 = \text{Al}_2(\text{SO}_4)_3 = 50.96 \\ \text{Free } \text{Al}_2\text{O}_3 \quad = 1.80, \text{ or} \\ \text{Al}_2(\text{SO}_4)_3 \quad = 50.96 \\ \text{Al}_2\text{O}_3 \quad = 1.80 \end{array} \right. \end{array}$$

In such reports the "combined" Al_2O_3 and also the $\text{Al}_2(\text{SO}_4)_3$, are calculated from the SO_3 present and the soluble so-called "free" Al_2O_3 is ignored as being of no value for sizing purposes. This idea that has so little, if anything, to support it, is discussed below.

A solution of normal sulphate of alumina behaves very much

¹ Read January 12, 1894.

like an acid; it combines with bases, evolves hydrogen with metals, and is acid to litmus paper. We should, therefore, expect SO_3 to combine with more alumina than is represented by the normal sulphate, and it might be added that as weak bases have the characteristic of forming basic salts, we should for this reason also anticipate the formation of basic sulphates of alumina. These basic sulphates can readily be formed in the laboratory from the normal sulphate.

1. By dissolving alumina in the normal sulphate.

2. By action of caustic alkalies on a solution of the normal sulphate. $\text{Al}_2(\text{SO}_4)_3 + \text{Na}_2\text{O} = \text{Al}_2\text{O}_3(\text{SO}_4)_2 + \text{Na}_2\text{SO}_4$.

For example: A solution of normal sulphate of alumina containing seven per cent. of alumina can be made two per cent. basic by adding caustic soda slowly to a hot solution until a precipitate forms that does not dissolve even on long boiling. This is equivalent in a seventeen per cent. material to having 4.86 per cent. in excess of that required to form $\text{Al}_2(\text{SO}_4)_3$.

3. By action of a metal, $\text{Al}_2(\text{SO}_4)_3 + \text{Zn} + \text{H}_2\text{O} = \text{ZnSO}_4 + \text{Al}_2\text{O}_3(\text{SO}_4)_2 + \text{H}_2$.

These equations are only intended to illustrate the probable types of reaction; it is not assumed that just such compounds are formed.

The following standard works treat of a number of basic sulphates of alumina that are soluble in water:

"Watts' Dictionary of Chemistry,"

"Roscoe & Schorlemmer's Chemistry,"

"Mendelejeff's Principles of Chemistry."

A careful search through the literature fails to reveal any reference to "free" alumina existing in a solution of normal sulphate.

The term "free" implies the reverse of combined and from the considerations given above it is not deemed best to call the alumina contents in excess of that required to form normal sulphate "free," with every condition favoring combination. Such alumina is undoubtedly combined as basic sulphate and being in solution there is every reason to believe that it would form a resinate of alumina with resin soap as readily as the normal sulphate, and some ground for the assumption that it might be even more available because it is probably held in weaker combination

and so would be more readily decomposed and precipitated as size; and if this were true such basic alumina would be more valuable than the normal because more would be precipitated by a given weight of resin soap. With these considerations in mind the following investigations were carried out in the laboratory. In order to observe the action of resin soap on a solution in which the alumina approaches nearest to the free state some aluminate of soda was prepared by dissolving alumina in caustic soda. In this solution alumina is so feebly held in combination that the weakest acids, such as carbonic, will replace it. The solution is basic, and alkaline to test paper.

Resin soap immediately precipitates a voluminous precipitate of resinate of alumina. Even upon the addition of a drop or two of resin soap the precipitate begins to form.

A comparison of a neutral sulphate containing seventeen per cent. soluble alumina and of a basic sulphate containing seventeen per cent. total soluble alumina, fifteen per cent. being normal and two per cent. being basic, the so-called "free," were each treated with an equal amount of resin soap in such quantity that but a portion of the alumina was precipitated. The solutions were filtered and precipitates washed with equal amounts of water and ignited. It was found that under such conditions

4.40 grams were precipitated from the neutral solution,
6.98 grams were precipitated from the basic solution.

These results are what theory would anticipate.

A brief summary of the case is this: It would seem that there is no "free" soluble alumina in the basic sulphate of alumina of commerce; such alumina is in direct combination as basic sulphate and being more feebly held in combination than alumina combined as normal sulphate, more readily forms size with resin soap and is therefore more economical, less resin soap being required for a given weight of sulphate. It directly follows from this that in any sulphate of alumina the $Al_2(SO_4)_3$ should be calculated from the total soluble alumina and *not* from that combined as normal sulphate alone, as in the latter case the most valuable alumina content is ignored as being useless. The following example will serve to illustrate the difference in value based on the two types of analyses: In a sulphate of alumina analyzing

| | |
|--|-----------------|
| Total soluble alumina..... | 17.00 per cent. |
| Alumina combined as normal..... | 15.20 " " |
| Basic alumina = so-called "free" | 1.80 " " |

The $\text{Al}_2(\text{SO}_4)_3$, calculated from 15.20 per cent. of alumina equals 50.96 per cent., whereas if calculated from 17.00 per cent. the $\text{Al}_2(\text{SO}_4)_3$ equals 57.00 per cent. In conjunction with these figures it must be borne in mind that experiment proves the basic sulphate of alumina to be relatively even more efficient than the difference in the above interpretations of analysis indicate.

DROPPING FLASK FOR STANDARD SOLUTIONS.¹

BY FRANK VANDERPOEL.

IT is well known that in working with standard solutions, the strength of the latter, when determined by the volume used, is influenced by the temperature to quite an appreciable extent. In fact, if a solution be standardized at 25° C. and afterward used at 20° C., its strength at the latter temperature is 1.001 times what it was at the former. For this reason it is necessary when employing volumetric apparatus to note the temperature of the solutions if very accurate work be done.

Again it has been observed that burettes and delivery pipettes sometimes vary in the volume of liquid delivered, this variation depending upon the nature of the solution or the ease with which it wets the sides of the glass tube, as all solutions are not the same in this respect.

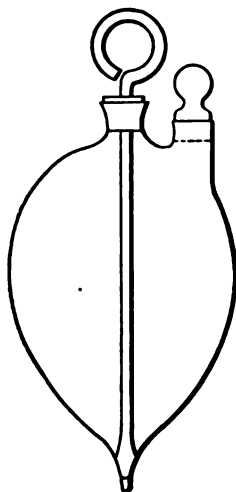
With an apparatus so made, however, that the standard solution is weighed instead of measured, these objections disappear, while accuracy is not impaired; in fact, with a common balance, sensitive to one centigram, much finer work can be done by weighing the solution than by measuring with a burette which reads to tenths of a cubic centimeter.

A number of dropping flasks and bottles have been invented from time to time with the above object in view; the one here represented having been devised some four or five years ago and kept in constant use in my laboratory ever since. It is quite simple and consists of a cylindrical or globular flask provided with two openings at the top and a dropping tube at the bottom

¹ Read December 8, 1893.

into which a glass rod is ground so as to make a tight joint. The rod runs through a perforated stopper in the central opening at the top in order that it may be kept in proper position. The second opening at the top is used when it is necessary to fill the bottle.

The apparatus may be supported by a small light tripod upon the pan of the balance, or it may be provided with two small hooks of brass wire fastened to a collar of the same metal which encircles the upper central tubulus. By means of these hooks the bottle is easily and quickly suspended from the bows supporting the balance pans.



I make use of a common pulp scale with four inch pans, and after counterpoising the filled bottle by means of brass cup weights supplemented by fine shot, perform the titration, and upon its completion determine the amount of liquid used by adding weights to that side of the balance from which the bottle is suspended. This necessitates but one calculation. The bottle

may be used for solution of potassium permanganate or silver nitrate or in fact any solution which is generally employed in a burette furnished with a glass stop-cock.

It is very readily taken apart, cleaned and dried.

NEWARK, N. J.

ON THE ESTIMATION OF POTASSIUM IODIDE AND SODIUM ACETATE IN THE PRESENCE OF COMPLEX ORGANIC MIXTURES.¹

BY JAMES H. STEBBINS, JR., PH.D.

I RECEIVED a short time since a sample of medicine for examination, which on qualitative analysis was found to contain potassium iodide and sodium acetate, together with certain complex vegetable extracts, and as the determination of the first two named compounds gave me a great deal of trouble before a

¹ Read January 19, 1894.

satisfactory method of analysis was found, I thought that an account of the process finally adopted, though containing no great novelty, might be of assistance to some of my colleagues should they ever by chance have to examine a mixture of this kind.

Potassium Iodide.—This compound was determined as follows without any trouble:

Ten cc. of medicine were diluted with 100 cc. of distilled water, and the salmon colored flocculent precipitate formed collected upon a filter.

After thoroughly washing the filter out with cold water, the iodine in the filtrate was determined as usual as iodide of silver and then calculated to iodide of potassium. The amount of the latter compound found was 3.58 per cent.

Sodium Acetate.—It was first sought to determine the acetic acid in the mixture as such in the usual way, by distillation with sulphuric acid, and from the quantity so found to calculate the percentage of sodium acetate present, but it soon became evident that this process could not be used, as the sulphuric acid was found to liberate iodine as well as acetic acid whose estimation was thus rendered impossible.

It was next sought to arrive at the percentage of sodium acetate by an examination of the ash left after igniting the dry extract. But unfortunately the usual method of incineration was found to be of no avail, as by this process the sodium acetate is either wholly or partially converted into sodium carbonate, no uniform products being obtainable, and the potassium iodide is likewise subject to decomposition and volatilization. Moreover it was found impossible to obtain an ash absolutely free from carbon, it always being necessary to treat the ash after ignition with water to free it from a small carbonaceous residue and then to ignite this residue a second time, to add its ash to the aqueous solution, to evaporate the whole to dryness, and to determine the per cent. potassium and sodium present as sulphates by the well-known process of indirect analysis.

As, however, no satisfactory conclusions could be reached in this way the following method was finally adopted:

Ten cc. of fluid extract were pipetted off into a capacious platinum dish and mixed with thirty cc. of twenty per cent. sulphuric

acid. The contents of the dish was now evaporated upon a steam bath to the consistency of a thick syrup. The dish was then transferred to a sand bath and gently heated until the contents had charred and no more fumes of sulphuric acid or iodine were given off. A compact carbonaceous mass will thus be obtained, which contains all the sodium and potassium in the fluid extract as sulphates. The contents of the dish were now moistened with ammonium nitrate solution evaporated to dryness over the steam bath, and then ignited over the direct flame of a Bunsen burner.

The carbon will in this manner be completely consumed, leaving a perfectly white residue of sodium and potassium sulphates, which are then further examined by the process of indirect analysis.

In the present case the sum of the sulphates of potassium and sodium, from ten cc. of fluid extract, was 0.2499 gram.

The amount of SO_3 contained in the 0.2499 gram of sulphates was 0.1208 gram, or equivalent to:

| | |
|-------------------------|----------------|
| Sodium sulphate | 0.57 per cent. |
| Potassium sulphate..... | 1.92 " " |

On now calculating the sodium sulphate to sodium acetate, and the potassium sulphate to potassium iodide, we get:

| | |
|------------------------|----------------|
| Sodium acetate..... | 0.65 per cent. |
| Potassium iodide | 3.65 " " |

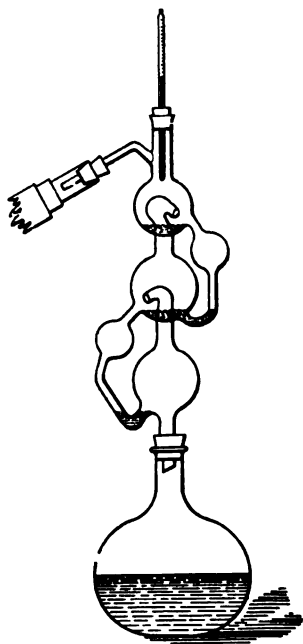
In the direct determination of the potassium iodide, as iodide of silver, we obtained 3.58 per cent. potassium iodide; hence it will be seen that the agreement between the direct and indirect methods of analysis is considering the complexity of the mixture under examination very satisfactory.

NEW YORK,
NOVEMBER 19, 1893.

APPARATUS FOR FRACTIONAL DISTILLATION¹

BY C. W. VOLNEY.

THIS apparatus for fractional distillation of mixtures of liquids of different boiling points is constructed on the



dephlegmator principle. Although the opening of the recurved main tube is never closed by the condensed liquid, comparatively only small quantities of vapors of the liquids, condensable in the respective bulbs, ascend or ultimately escape in the condenser, so that by a second distillation liquids of practically uniform boiling points are obtained.

I have used this apparatus for the preparation of paraffins and benzene derivatives, and can recommend it as a good and practical instrument. The principle employed is evident from the figure, and any glass blower can make it.

NEW YORK,
NOVEMBER 23, 1893.

¹ Read December 8, 1893.



THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(Continued from 15, 181, 1893.)

BY THOMAS B. STILLMAN, PH.D.

NO standard specifications for the testing of Portland cement are required in Great Britain, the determination of fineness, tensile strength and variations in volume, being considered sufficient to determine the value of a cement. The machines for

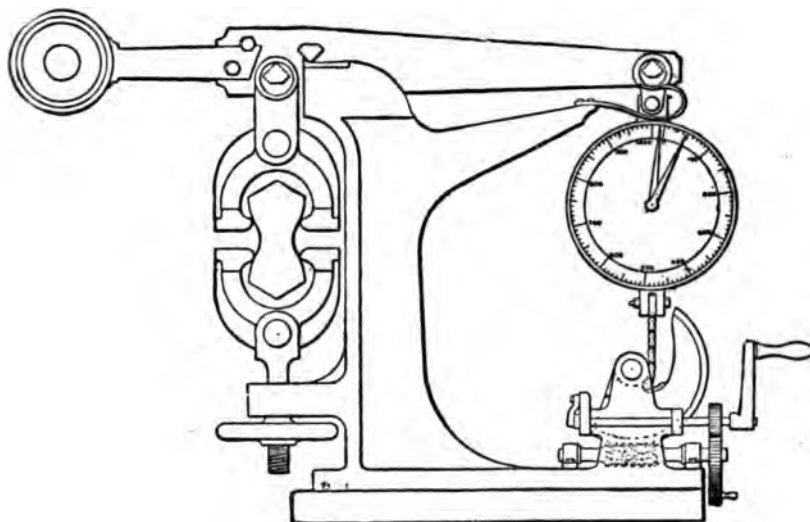


Fig. 5.

tensile strength are the "Faija" (Fig. 5), the "Reid and Bailey" (Figs. 6 and 6a), or the "Grant," the latter described in *Proceedings* of the Institution of Civil Engineers, **62**, 113. The "Reid and Bailey" is essentially the "Michaelis" (Fig. 4), excepting that water is used instead of fine shot for the breaking power.

It is readily seen that the "Faija" and "Grant" machines, not being automatic, require the application of the power at a certain uniform speed to obtain comparable results, since a difference of twenty-five per cent. in tensile strength may be obtained by applying the strain very quickly or very slowly (*Proceedings* of the Institution of Civil Engineers, **75**, 225, 226).



Fig. 6.



Fig. 6a.

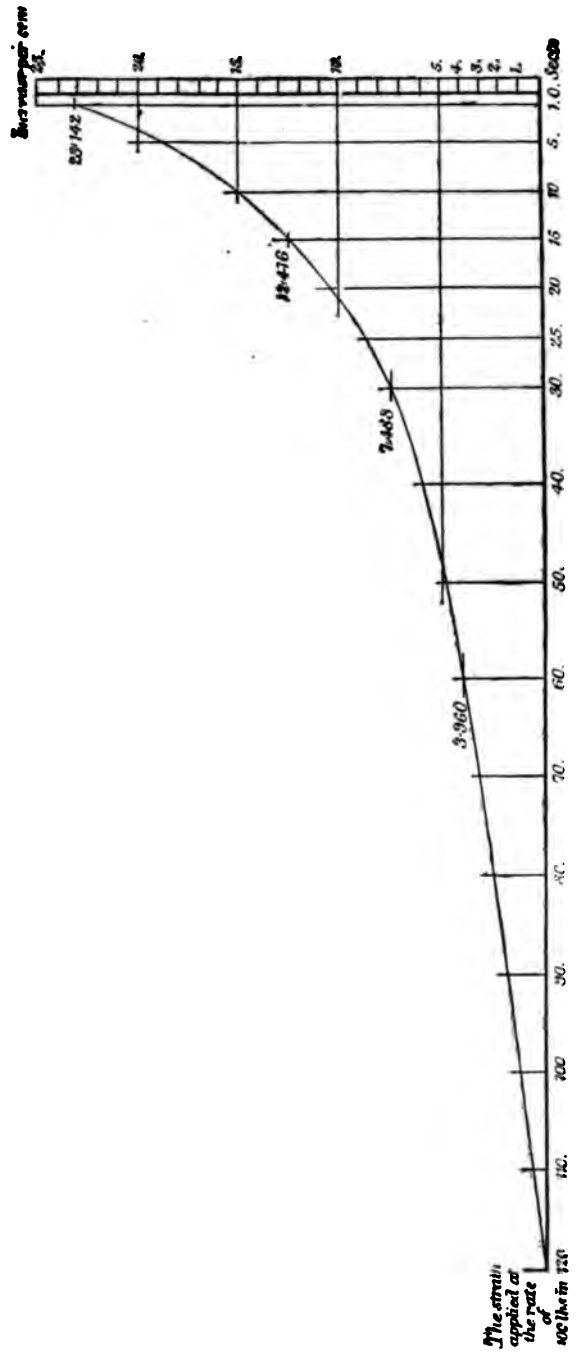


Fig. 7.

Faija has determined this variation with extreme care, the result being indicated in the curve shown in Fig. 7. To overcome these variations a uniform speed of 400 pounds per minute has been accepted as the standard.

Not only are comparable methods required in the use of the machines to obtain uniform results, but the briquettes must also be constructed under similar conditions.

It is manifestly unjust to compare the tensile strength of two cements (even when the briquettes are broken upon the same machine) unless the briquettes have the same weight of water for mixing; the same pressure with the trowel when being formed in the molds, and the same length of time of exposure under water before submitting the briquettes to the tensile strain. Usually the greatest difference is due to the pressure exerted in forming the briquettes.

For instance: Comparing tests made upon the Dyckerhoff Portland cement by Dr. Böhme, Director of the Royal Commission for testing building materials, at Berlin, and by E. J. De Smedt, General Inspector Engineer Department, District of Columbia, we find that the German method gives a much higher tensile strength than the method in use in this country.

| DR. BÖHME. | | |
|-----------------------|---|------------------|
| Age of Briquettes. | Average tensile strength per square inch. | Number of tests. |
| 7 days..... | 767 pounds | 10 |
| 28 " | 895 " | 10 |
| E. J. DE SMEDT, C. E. | | |
| Age of briquettes. | Average tensile strength per square inch. | |
| 5 days..... | 250 pounds | |
| 30 " | 700 " | |

Showing:

109 pounds increase per day (7 days), Dr. Böhme,
50 " " " " (5 days), De Smedt,

or over 100 per cent. difference upon the same cement.

These variations are undoubtedly due principally to the different pressures upon the cement during the making of the briquettes, and to overcome difficulties of this nature the Vereins deutsche Portland Cement Fabrikanten have modified the rules in the construction of the briquettes so that two methods are acceptable:

First. The normal method, above given, with the trowel, etc., ("Handarbeit").

Second. The use of the Böhme-Hammer apparatus or "machine method," by which the cement in the briquette form

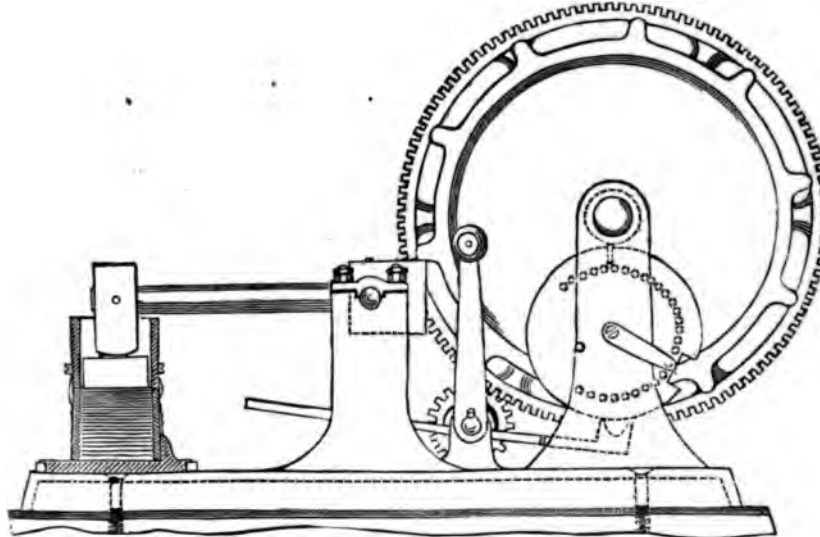


Fig. 8.

(after mixing with proper amount of water), is submitted to a pressure of 150 blows from a hammer weighing two kilos (Fig. 8). The briquette of cement is then removed from the mold and treated for tensile strength as usual.

This subject is receiving considerable attention at the present moment, the evident purpose being to render the tests of tensile strength as uniform as possible by making the working of the apparatus automatic and the production of cement briquettes with the least possible variation in the pressure in the molds.

In this case, no matter how careful the experimenter may be, the "personal equation" enters largely into the results of testing hand-made briquettes, for which reason the manufacture of the briquettes should be as automatic as possible. In no other way can results obtained by different experimenters be compared.

Prof. Charles D. Jameson describes an apparatus for this purpose (Fig. 9). *Transactions of the American Society of Civil Engineers*, **25**, 302.

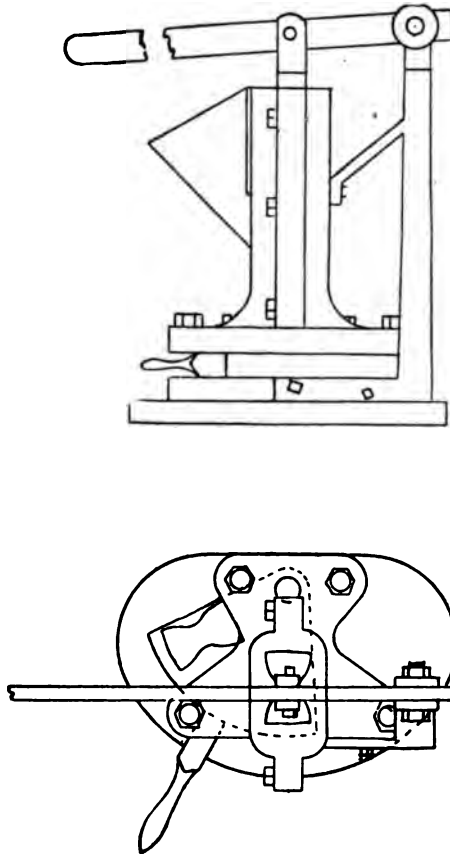


Fig. 9.

The method of operating is as follows: The lever being raised so that the lower end of the piston or main plunger is above the hole in the side of the cylinder communicating with the hopper, cement is put in the hopper and pushed down into the cylinder. The molding plate is pushed against one of the stops, so that one of the openings is beneath the bore of the cylinder. The long lever is forced down, causing the

plunger to force the cement into the opening in the molding plate. After this, the molding plate is swung against the other stop, cutting off the briquette, placing it over the plungers, throwing the other opening in the molding plate directly beneath the cylinder. The smaller lever is lifted, raising the plunger, and forces the briquette out of the mold, after which it is removed. The plunger is then pressed down, the main lever also, the molding plate swung back to the first position, the other plunger lever lifted, and another briquette is ready to be taken away, and so on. After making three briquettes, the main lever is lifted and more cement placed in the cylinder. The machine is best operated by two men, one to feed and operate the long lever, and the other to swing the molding plate, remove the briquettes, and lower the plungers. The pressure on the briquette is 175 pounds per square inch.

The conditions required in France for a good cement are:¹

First. Analysis to determine the chemical composition.

Second. The determination of density.

Third. The determination of fineness.

Fourth. The determination of tensile strength.



Fig. 10.

Fifth. The determination of crushing strength.

¹ E. Candlot, *Ciments et Chaux Hydrauliques*, Paris, Baudry and Co., 1891.

Sixth. The determination of variations in volume.

The tensile strength is determined by the use of a Michaelis machine, Fig. 10, or the use of a Buignet apparatus, Fig. 11, this latter being upon an entirely different principle than any yet in use, and is thus described by the designer, M. Buignet, Conductor des ponts et chaussées au Havre :

It is composed of a basin A and frame B.

The basin A, filled with mercury and water, closes up by a diaphragm of rubber covered with a metallic disk, and is in direct communication with:

- (a) Manometrique tube D.
- (b) With a movable reservoir R, filled with mercury, by means of a rubber tube T.

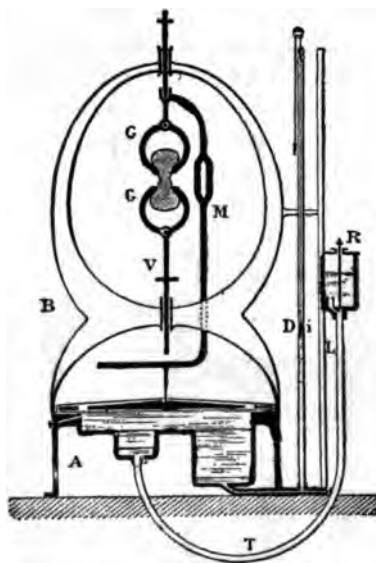


Fig. 11.

The grips G G, in which are to be placed the briquettes to be tested, are fastened, one to the frame B by the support V, the other to the support M, which rests upon the center of the metallic disk over A. It is operated as follows: The briquettes are placed in the grips G G, and the support V moved up or

down until equipoise is established, and then firmly secured by a crank in frame B.

The support M is adjusted until the point at its lower end just touches the metallic disk in A.

By gradually lowering the reservoir R an upward pressure is given to the metallic disk in A, which is transferred to the support M, until when sufficient pressure is exerted the briquette is broken. The moment rupture of the briquette takes place, the pressure required to do this is indicated by the float *i* in the manometer tube D.

Another instrument made use of to determine tensile strength, and used at l' école des ponts et chaussées, Paris, is shown in Fig. 12.

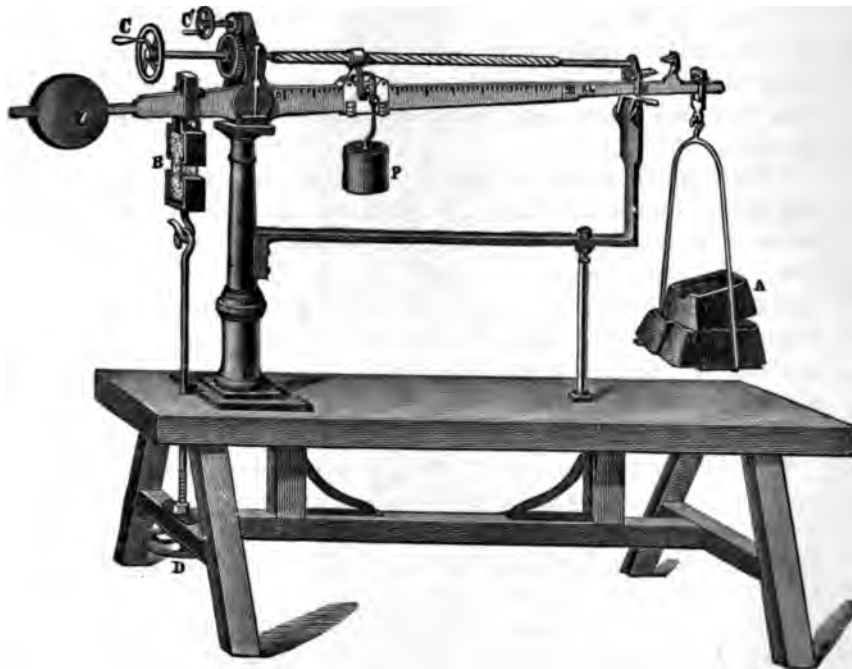


Fig. 12.

It is similar in principle to the Riehle machine (Fig. 2), and the Grant machine (*Proceedings of the Institution of Civil Engineers*, 62, 98).

By a comparison of the various machines used in Germany, England, France, and the United States, we find practically but two in general use. The "Michaelis" (Figs. 4, 10, and 1), and the "Grant" (Figs. 2 and 12). While nearly all engineers require cements to be subjected to the tensile strength test, in fact relying more upon this one test than any of the others, it might be well to include here the opinion of H. Le Chatelier, professor at the École des Mines, Paris, France, as given in a paper presented at the last meeting of the American Institute of Mining Engineers, August, 1893, entitled "Tests of Hydraulic Materials," p. 44.

"The method of tension is at present most widely used, but the preference for it is not well founded.

"Here, as in rupture by bending, only the *surface* of the briquettes acts in a really useful way, and its inevitable irregularities and alterations so greatly affect the precision of the results that they can in no case be trusted nearer than about twenty per cent.

"This preponderant influence of the superficial parts was first shown by the fact that the resistance of briquettes of different sizes increases, not with the section, but, on the contrary, with the perimeter. Finally, M. Durand-Claye has shown that the interior of a briquette may be removed without notably diminishing its resistance to rupture by tension, and has given a complete theoretical explanation of the phenomena which seemed at first sight paradoxical."

THE CRUSHING TEST.

This test is not official in this country and is seldom required by our engineers, who, however, have confined their experiments in this direction mainly to crushing tests of concrete, formed by mixing Portland cement, sand, and broken stone.

Tests upon cubes of neat cement and of mortar composed of one part cement and three of standard sand, are generally included in reports given upon the examination of cements in Europe, the ratio being that the crushing strength is about ten times greater than the tensile strength.

Thus, a cement of good quality should show the following resistances per square centimeter:

TENSILE STRENGTH.

| | 7 days. | 28 days. |
|-----------------------|----------|----------|
| Neat cement | 25 kilos | 35 kilos |
| 1 part cement } | 10 " | 18 " |
| 3 parts sand } | | |

CRUSHING STRENGTH.

| | 7 days. | 28 days. |
|-----------------------|-----------|-----------|
| Neat cement | 250 kilos | 350 kilos |
| 1 part cement } | 100 " | 180 " |
| 3 parts sand } | | |

To convert kilos per square centimeter to pounds per square inch, the equivalents used are: one kilo = 2.204 pounds English; 6.451 square centimeters = one square inch English.

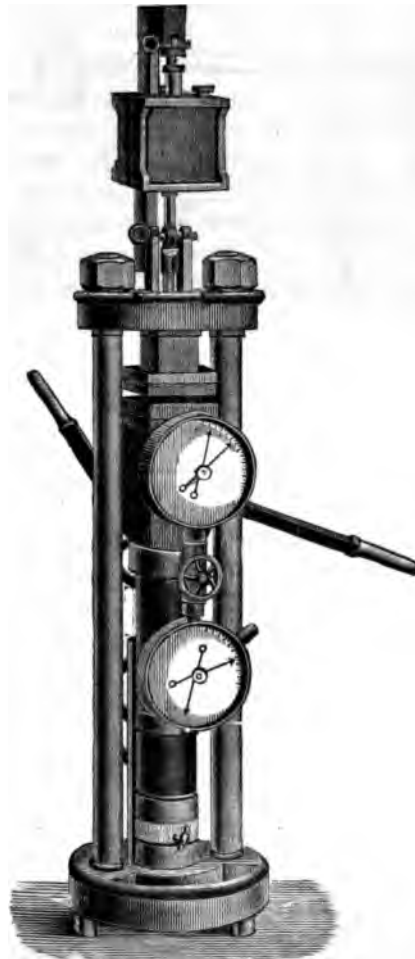


Fig. 14.

The hydraulic presses made use of for this purpose, a few years since, gave very discordant results, as it was impossible to distribute the pressure evenly over the surface of the cubes. This has been overcome, and there are now four machines upon the market whose results are comparable, *viz.* :

The "Suchier," Fig. 14; the "Böhme," Fig. 15; the "Tetmajer," as improved by Prof. Amsler-Laffon,¹ and the "Brink and Hubner."²

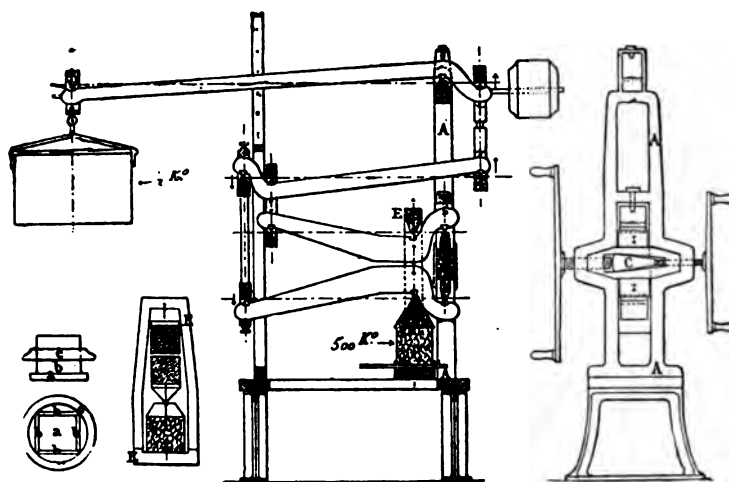


Fig. 15.

Variation in volume (expansion or contraction).—The method of Faija³ the one generally used for this purpose is as follows :

Three pats should be made on pieces of glass or other non-porous substance, and their behavior watched under the following conditions :

Pat No. 1 may be left in the air, and No. 2 should be put in water as soon as it is set hard.

Pat No. 3 should be treated in the apparatus for determining

¹ Consult : *Schweizer Bauzeit*, January 12, 1889.

² Description of the "Suchier," "Böhme," and "Brink and Hubner" machines will be found in *Der Portland Cement und seine Anwendungen im Bauwesen*, Berlin, 1892.

³ The determination of liability to "checking" or "cracking" (variation in volume) in Portland cements as recommended by *American Society Civil Engineers*, is not as complete as Faija's method, see this JOURNAL, 15, 184.

the soundness of cement. The apparatus consists of a covered vessel in which water is maintained at an even temperature of 110°C ; the space above the water is therefore filled with the vapor rising therefrom, and is at a temperature of about 100°C . Immediately the pat is gauged, it should be placed on a rack in the upper part of the vessel, and in five or six hours it may be placed in the warm water and left therein for nineteen or twenty hours. If, at the end of that period, the pat is still fast to the glass and shows no signs of blowing, the cement may be considered perfectly sound; should, however, any signs of blowing appear, the cement should be laid out in a thin layer for a day or two, and a second pat made and treated in the same manner, as the blowing tendency may only be due to the extreme newness of the cement.

If pat No. 3 shows the cement to be unsound, pats No. 1 and 2 will eventually prove it, but it may be weeks or even months before they develop the characteristics. If pat No. 2 blows, it may be because it was put in the water before it was set. A cement is considered set hard when it can no longer be marked by the pressure of the thumb nail.

Résumé:

The determination of the value of Portland cement therefore requires the following tests:

First. Chemical analysis.

Second. Determination of fineness.

Third. Determination of tensile strength, including the use of automatic briquette machines as well as an apparatus for mixing the cement with water, as "Faija" mixing machine.

Fourth. Determination of crushing strength.

Fifth. Determination of variation of volume.

RECENT PROGRESS IN THE ANALYSIS OF CATTLE FOODS.¹

By F. W. WOLL.

OUR methods of analysis of cattle foods are essentially the Weende methods, published nearly thirty years ago in *Landw. Versuchs Stationen*, **6**, (1864,) 496, by Henneberg. An outline of the methods as given in the place cited, will at once show this to be true.

Henneberg gives the following directions for the determination of the various components of fodders.

1. *Water*.—A few grams of the finely powdered, air-dry sample are heated at 100–110° C., and the results calculated on the original substance.

2. *Mineral Matters* (ash excluding carbon dioxide).—100 to 200 grams are ignited in a muffle oven at as low temperature as possible, and the crude ash weighed, carbon dioxide and char are then determined in a portion of the crude ash, and corrections made accordingly.

3. *Protein*.—Determination of nitrogen and using the factor 6.25.

4. *Crude Fiber*.—A quantity corresponding to three grams water-free substance is taken, and heated for one-half hour in a flat porcelain dish with 200 cc. of a 1½ per cent. sulphuric acid solution, adding water as it boils away; the solution is then left to settle and the clear liquid pipetted off into a beaker; the sample is again boiled for one-half hour with water, the clear liquid pipetted off into the same beaker as before, and the operations of boiling with 200 cc. of water and pipetting off repeated a second time. 200 cc. of a 1½ per cent. potassium hydroxide solution are then added and boiled for half an hour, the clear liquid pipetted off into a second beaker, the residue boiled twice with 200 cc. of water, each time uniting the liquid with that already in the second beaker. The residue is then brought on a filter and also that which has settled in the beaker containing the alkaline fluid; the filter is washed until neutral reaction, when the residue in the other beaker is added and the washing repeated and finished by

¹ Read before the World's Congress of Chemists, August 24, 1893.

successive washings with alcohol and ether, drying, weighing, and incineration, which gives the crude fiber by difference.

5. *Ether Extract* (fat).—Complete extraction with boiling anhydrous ether, distillation of the united filtered distillates, and drying the residue at 100–110° C.

Since these methods were first published, our knowledge of the composition of plants and feeding stuffs has been greatly widened; we understand far better than did the writers thirty years ago, what the various groups separated out by the Weende experimenters include, and the conditions which must be observed in each case in order to obtain correct results. But on the purely analytical side we have made but very little progress; the problems have grown more complex every year, and the difficulties of the problems have increased much faster than has our ability to meet them.

In giving a short account of the progress made during recent years in the analysis of cattle foods, I shall take up the various components in the order adopted by Henneberg and still followed by agricultural chemists in general, and shall show the changes which the methods have undergone and suggest the reason for these changes.

As shown by Wilm, Bahring, Baessler, and others, *moisture* cannot be determined in many of our food stuffs by a simple drying in the air, as the fat contained in them will oxidize and the sample thus increase in weight, which means a too low percentage of moisture. Desiccation must, therefore, be conducted in the medium of an indifferent gas; the gas now generally adopted for drying is hydrogen or carbon dioxide, preferably the former. Märcker has further shown that drying above 100° C. may cause formation of resinous substances, and Jenkins found that a volatile oily matter passed off when fodders were heated at 110° in the air or in other gases; the same was observed by Baessler, Wiley, and Cutter. The temperature ought, therefore, never to exceed 100° C. The time necessary for drying will depend on the kind of apparatus used and will vary from four to ten hours; in case of a dry current of hydrogen being passed through the samples, four to six hours will as a rule be found necessary, the velocity of the current being the deciding factor

as to the time required; 90 to 100 bubbles of hydrogen per minute is a maximum velocity (Anderson). The loss of volatile substances will be increased when a very rapid current is passed through the sample. Where the fodders are heated on watch glasses or in open disks in an atmosphere of hydrogen, longer time will be necessary than otherwise, sometimes as much as ten hours, the temperature of drying being all the time that of boiling water.

Ether Extract.—The determination of ether extract has been greatly facilitated by the adoption of the Soxhlet continuous extraction apparatus; the form of extraction tube generally used in the United States is the Johnson extractor, the most recent modification of this being the Caldwell extractor.

The ether extract is determined in the water-free sample, as the air-dry sample extracted with ether will give too high results, for obvious reasons. The ether to be used for extraction must be anhydrous and alcohol-free, as too high results will otherwise be obtained. Numerous comparisons of extraction with ether of different kinds and under varying conditions of drying previous to extraction, have been made by Atwater, Babcock, Wilm, Bahring, Wagner, Märcker and scores of others, and the above points have been fully settled.

As there are several reasons for believing that prolonged drying of any food stuff even at 100° C. modifies the solubility of the fat and the amount of ether extract found, the writer has recently proposed the use of anhydrous copper sulphate in ether extraction. The sulphate will dehydrate both fodder and ether used, and no special precautions for dehydration of either are necessary. The sample of 2-3 grams weighed out may be mixed with about five grams of copper sulphate and the mixture placed in the extraction tube and extracted as usual.

Stellwaag's and Maxwell's investigations have shown the complexity of the bodies making up the ether extract of most feed stuffs. The former found from 0.5 to 34.6 per cent. of insaponifiable components in twenty-five common fodders; lecithin, cholesterin, and hydrocarbons have been shown to be present in many cases, as well as coloring matters. It is especially the ether extracts of coarse fodders and roots which contain large pro-

portions of non-glycerides; the extracts of seeds of all kinds are as a rule fairly pure. Various methods have been proposed for the purification of the crude fat, but none have been generally adopted. The purification by means of animal charcoal, proposed by G. Kühn, nearly twenty-five years ago, and proved inaccurate by König in 1871, and by Schulze in 1872, was brought forward again a few years ago by Patterson, who obtained correct results with it. By more recent, thorough investigations it has been shown, however, that animal charcoal will retain fat from ethereal solutions passing through it. There is considerable difference in this respect between different kinds of charcoal, making the method entirely unsatisfactory in quantitative analysis.

Crude Protein is determined by multiplying the per cent. of nitrogen found by the Kjeldahl method by 6.25. A great step in advance was made in the adoption of this method (pub. 1883) in agricultural laboratories, and also in the separation of crude protein into albuminoids and amides, according to Stutzer's copper hydrate method (pub. 1880). The Kjeldahl method has been modified by a large number of chemists, and also so as to include nitrate nitrogen; the latter modifications most adopted are those of Jodlbauer and Ulsch.

Crude Fiber.—The Weende method is still the one used by most agricultural chemists. Schulze's method (pub. 1866) and Höning's (pub. 1891) have both been proved unreliable by several chemists; but on the other hand the investigations made have also proved conclusively that the Weende method gives too low results, contrary to the experience of Kühn and Kern. In comparative determinations the results by the Weende method have come lower in every case, being often only one-half or two-thirds of those found by the Schulze or Höning method in case of our ordinary cattle foods. It cannot, therefore, be denied that we are still without a satisfactory method for the determination of cellulose or crude fiber in fodders, and use the Weende method only for want of something better.

Ash is determined in a small quantity of the fodder at the present time, not exceeding ten grams. The manner of procedure is otherwise as in the Weende method; or the sample is

carefully burned at a low red heat, the crude ash treated with water, filtered, the residue ignited to whiteness, united with the filtrate, which is then evaporated and the residue heated to low red heat. The reason for this method of proceeding is the easy volatilization of chlorides by direct heating of the ash above red heat, which is necessary to burn the carbon of the ash.

Nitrogen-free Extract is determined by difference, as directed by Henneberg. The errors of analysis incident to the determination of all other components, therefore, enter here and often make the results unsatisfactory. The heterogeneous character of the bodies coming in under this head makes it unfortunate to class all together. A great deal of study has been expended in separating and identifying the various constituents of the nitrogen-free extract of fodders. Pentosans, as galactose, arabinose, xylose were discovered in cattle foods some years ago by Tollens, Schulze and their assistants, and have been found in appreciable quantities in nearly all our common food stuffs. While no satisfactory quantitative method for their determination has yet been devised, the furfurol reaction, worked out by Stone, Allen, and Wheeler, gives a very sharp qualitative test for them.

If determinations of sugar, starch, and possibly also pentosans, could be made in our cattle foods, the rest of the nitrogen-free extract could be classed as *undetermined* and would then include many bodies present in all fodders, the properties of which we yet know very little about, and whose nutritive value is perhaps inferior.

From this short sketch we readily see that more progress has been made in our knowledge of the composition of food stuffs, and in the identification of these constituents than in their estimation. While brought to a certain perfection as far as working details go, the analytical side is yet far behind, and no fully satisfactory system of fodder analysis can be worked out until we are able to classify nutrients more according to their physiological importance than is done in our present methods.

REPORT OF COMMITTEE ON DETERMINATIONS OF ATOMIC WEIGHT, PUBLISHED DURING 1893.¹

BY F. W. CLARKE.

To the Members of the American Chemical Society:

YOUR committee, appointed at the last annual meeting, respectfully submits the following report, showing the advances made in our knowledge of atomic weights during 1893. The year has been one of reasonable activity in this branch of investigation, and it is thought that all the work actually published within its limits is here summarized and recorded. One partial exception possibly may be made to this statement. Morley's work on oxygen, reported orally at the American Association meeting, and at the Chemical Congress in Chicago, is omitted, for only unofficial abstracts of it have yet appeared in print. That work is of such fundamental importance that it seems best to await its completion, rather than to do it possible injustice by fragmentary notices which might be inexact.

In the "Stas Memorial Lecture," by Professor Mallet,² will be found a remarkably full discussion of the theory or philosophy of atomic weight determinations, which should be carefully read by all students in this domain. Taking the life and work of Stas as text and example, Mallet considers the conditions necessary to the fruitful continuation of that work, and throws out many suggestions of great practical value. He particularly advocates the multiplication of interdependent data, in order that errors may be eliminated; and he also recommends the establishment of a special, endowed laboratory, in which a group of trained observers may co-operate towards the attainment of the best results.

The individual atomic weight determinations of 1893 are subjoined.

Boron.—W. Ramsay and Emily Aston³ redetermine the atomic weight of boron by two distinct processes, one of them being entirely new. First, with many precautions, they estimate

¹ Read at the Baltimore meeting Dec. 28, 1893.

² *J. Chem. Soc.*, August, 1893.

³ *J. Chem. Soc.*, 63, 207, February, 1893.

the percentage of water in crystallized borax, $\text{Na}_2\text{B}_4\text{O}_{10} \cdot 10\text{H}_2\text{O}$; all weights being reduced to vacuum standards. The same reduction is also made in their other series, but as they carry out the weights to seven decimal places, the corrections applied go farther than is necessary. In the subjoined tables I give the nearest tenth milligram.

| Wt. $\text{Na}_2\text{B}_4\text{O}_{10} \cdot 10\text{H}_2\text{O}$. | Wt. $\text{Na}_2\text{B}_4\text{O}_7$. | Per cent. H_2O . | At. Wt. B. |
|---|---|----------------------------------|------------|
| 10.3582 | 5.4784 | 47.1099 | 11.04 |
| 5.3440 | 2.8247 | 47.1433 | 10.97 |
| 4.9963 | 2.6379 | 47.2026 | 10.85 |
| 5.7000 | 3.0101 | 47.1912 | 10.87 |
| 5.3143 | 2.8066 | 47.1882 | 10.88 |
| 4.9972 | 2.6392 | 47.1865 | 10.885 |
| 5.2367 | 2.7675 | 47.1524 | 10.955 |

Mean atomic weight, $B=10.921, \pm 0.010$.

In the second series of experiments fused borax was distilled with hydrochloric acid and methyl alcohol, and the residual sodium chloride was weighed. Results as follows:

| Wt. $\text{Na}_2\text{B}_4\text{O}_7$. | Wt. NaCl . | At. Wt. B. ¹ |
|---|---------------------|-------------------------|
| 4.7684 | 2.7598 | 11.015 |
| 5.2740 | 3.0578 | 10.925 |
| 3.2344 | 1.8727 | 10.992 |
| 4.0862 | 2.3713 | 10.879 |
| 3.4970 | 2.0266 | 10.949 |

Mean atomic weight, $B=10.952, \pm 0.010$.

The distillations were conducted in soft glass flasks of about 100 cc. capacity, in which the sodium chloride was dried at about 350° , and finally weighed. It was found, however, that the flasks were somewhat attacked during the process, with liberation of silica, consequently some oxygen in the alkali of the glass had been replaced by chlorine, and the weight of the vessel increased. Another set of distillations was, therefore, made with flasks of hard combustion tubing, and these were slightly attacked also.

| Wt. $\text{Na}_2\text{B}_4\text{O}_7$. | Wt. NaCl . | At. Wt. B. |
|---|---------------------|------------|
| 5.3118 | 3.0761 | 10.983 |
| 4.7806 | 2.7700 | 10.955 |
| 4.9907 | 2.8930 | 10.936 |
| 4.7231 | 2.7360 | 10.968 |
| 3.3138 | 1.9187 | 10.992 |

Mean atomic weight, $B=10.966, \pm 0.005$.

¹ Atomic weights used in Ramsay and Aston's calculations: $\text{O}=16$, $\text{H}=1.008$, $\text{Ag}=107.92$, $\text{Na}=23.05$, $\text{Cl}=35.45$, and $\text{Br}=79.95$.

As a check upon these results the sodium chloride was dissolved in water, and after filtration precipitated with silver nitrate. The resulting silver chloride was collected on a Gooch filter, dried at 200°, and weighed.

| Wt. AgCl. | Per cent. Cl in NaCl. | At. Wt. B. from Cl. |
|-----------|-----------------------|---------------------|
| 7.5259 | 60.493 | 11.071 |
| 6.7794 | 60.515 | 11.024 |
| 7.0801 | 60.516 | 11.003 |
| 6.6960 | 60.514 | 11.039 |
| 4.6931 | 60.479 | 11.091 |

Mean atomic weight, $B=11.052, \pm 0.010$.

From all these results, and after discussing the supposable sources of error in them, the authors conclude that the atomic weight of boron is very nearly eleven.

Still another determination of the atomic weight of boron, by an entirely independent method, is due to Rimbach.¹ Taking advantage of the fact that methyl orange, as an indicator, is unaffected by free boric acid, he titrated solutions of borax with standardized hydrochloric acid, thus measuring the amount of sodium in the salt and thence calculating the value to be ascertained. The borax was prepared in platinum vessels from carefully purified boric acid and sodium carbonate; and the hydrochloric acid used contained 1.84983 per cent. of absolute HCl, determined gravimetrically as silver chloride. In the following table of results the titrated hydrochloric acid is given by weight in grams:

| Wt. borax. | Wt. HCl. sol. | Per cent. Na. ² | At. Wt. B. ² |
|------------|---------------|----------------------------|-------------------------|
| 10.00214 | 103.1951 | 12.07081 | 10.9646 |
| 15.32772 | 158.1503 | 12.07138 | 10.9598 |
| 15.08870 | 155.7271 | 12.07530 | 10.9273 |
| 10.12930 | 104.5448 | 12.07517 | 10.9298 |
| 5.25732 | 54.2571 | 12.07435 | 10.9361 |
| 15.04324 | 155.2307 | 12.07283 | 10.9486 |
| 15.04761 | 155.2959 | 12.07448 | 10.9356 |
| 10.43409 | 107.6602 | 12.07176 | 10.9571 |
| 5.04713 | 52.0897 | 12.07480 | 10.9330 |

Calculating from the sum of all the weights the atomic weight of boron becomes 10.945, ± 0.003 .

¹ *Ber. d. chem. Ges.*, 26, 164, February, 13, 1893.

² Calculations made with O=16, H=1.0032 (Kaiser), Na=23.0575, Cl=35.4529, and Ag=107.9376.

Carbon.—Leduc¹ has determined the density of carbon monoxide, deducing thence the atomic weight of carbon. The globe used held 2.9440 of air. Filled with carbon monoxide the latter weighed

2.8470
2.8468
2.8469

Mean, 2.8469

Hence the density of CO is 0.96702, when air = 1, and with

O = 15.88,
C = 11.913,

If O = 16, then C = 12.003.

In a very brief note² Wanklyn announces that he has studied a series of hydrocarbons in which the successive steps rise—not by $\text{CH}_2 = 14$ —but by $\frac{1}{2} (\text{CH}_2) = 7$. If these observations are sustained, then the atomic weight of carbon becomes = 6.

Cobalt and Nickel.—Atomic weights determined by Winkler,³ who starts with weighed quantities of metal, electrolytically deposited. This is then dissolved in a platinum dish in pure hydrochloric acid, and the chlorides produced are finally dried for several hours at 150° . In one set of experiments the chlorine in the chlorides is weighed gravimetrically, as silver chloride; in another set it is titrated with a standard solution of silver. In the first case we have the ratio $\text{R} : 2\text{AgCl}$, in the other, $\text{R} : \text{Ag}$. Results as follows, for nickel:

| Wt. Ni. | Wt. AgCl. (grav.) | At. Wt. Ni. |
|---------|-------------------|-------------|
| 0.3011 | 1.4621 | 58.9102 |
| 0.2242 | 1.0881 | 58.9418 |
| 0.5166 | 2.5108 | 58.8571 |
| 0.4879 | 2.3679 | 58.9419 |
| 0.3827 | 1.8577 | 58.9304 |
| 0.3603 | 1.7517 | 58.8334 |

Mean result, Ni = 58.9033.

| Wt. Ni. | Wt. Ag. (vol.) | At. Wt. Ni. |
|---------|----------------|-------------|
| 0.1812 | 0.6621260 | 58.9253 |
| 0.1662 | 0.6079206 | 58.8665 |
| 0.2129 | 0.7775252 | 58.9584 |
| 0.2232 | 0.8162108 | 58.8811 |
| 0.5082 | 1.8556645 | 58.9684 |
| 0.1453 | 0.5315040 | 58.8631 |

Mean result, Ni = 58.9104.

¹ *Compt. rend.*, 115, 1072.

² *Phil. Mag.*, (5) 36, 552, December, 1893.

³ *Ztschr. anorg. Chem.*, 4, 10, 1893.

The following data were obtained for cobalt:

| Wt. Co. | Wt. AgCl. (grav.) | At. Wt. Co. |
|---------|-------------------|-------------|
| 0.3458 | 1.6596 | 59.6044 |
| 0.3776 | 1.8105 | 59.6609 |
| 0.4493 | 2.1521 | 59.7215 |
| 0.4488 | 2.1520 | 59.6577 |
| 0.2856 | 1.3683 | 59.7081 |
| 0.2648 | 1.2678 | 59.7480 |

Mean result, Co=59.6834.

| Wt. Co. | Wt. Ag. (vol.) | At. Wt. Co. |
|----------|----------------|-------------|
| 0.177804 | 0.6418284 | 59.6495 |
| 0.263538 | 0.9514642 | 59.6396 |
| 0.245124 | 0.8855780 | 59.5996 |
| 0.190476 | 0.6866321 | 59.7311 |
| 0.266706 | 0.9629146 | 59.6388 |
| 0.263538 | 0.9503558 | 59.7092 |

Mean result, Co=59.6613.¹

In the case of the cobalt determinations it is of course conceivable that the chloride formed might be contaminated with traces of basic compounds. This question is considered by Winkler in a supplementary communication.² The weighed, electrolytic cobalt, deposited upon the surface of a platinum dish, was treated with a solution of neutral silver sulphate. Silver was thrown down, and was washed, dried, ignited, and weighed. Thus a direct ratio was measured between silver and cobalt, involving no intervention of cobalt chloride, and consequently no error due to basic salts. Results as follows:

| Wt. Co. | Wt. As. | At. Wt. Co. |
|---------|---------|-------------|
| 0.2549 | 0.9187 | 59.7421 |
| 0.4069 | 1.4691 | 59.6377 |

The precipitated silver, as a check upon its purity, was dissolved in nitric acid, reprecipitated with hydrochloric acid as chloride, and filtered off. The filtrate, upon evaporation to dryness, gave traces of residue, containing cobalt. The amount of the latter in the first experiment was at most 0.5 milligram, and in the second not over 0.2 milligram. Correcting for these amounts the values found for the atomic weight of cobalt become 59.6356 and 59.6164, respectively. These figures fall within the limits of variation of those found in the first paper.

¹ All calculations with Ag=107.66 and Cl=35.37

² *Ztschr. anorg. Chem.*, 4, 462, 1893.

and show that the supposed error, if it existed, could not be large. The author admits, however, that the degree of concordance among his experiments is not so great as could be desired. The main purpose of his work was to show the essential constancy of the values, as opposed to the views of Krüss concerning the supposed composite nature of nickel and cobalt.

Molybdenum.—Atomic weight redetermined by Smith and Maas.¹ Sodium molybdate was converted into chloride by heating in a current of pure, dry, gaseous hydrochloric acid. Results as follows with weights reduced to vacuum standards:

| Wt. Na_2MoO_4 . | Wt. NaCl . | At. Wt. Mo . |
|---------------------------------|---------------------|-----------------------|
| 1.14726 | 0.65087 | 96.130 |
| 0.89920 | 0.51023 | 96.094 |
| 0.70534 | 0.40020 | 96.108 |
| 0.70793 | 0.40182 | 96.031 |
| 1.26347 | 0.71695 | 96.087 |
| 1.15217 | 0.65367 | 96.126 |
| 0.90199 | 0.51188 | 96.067 |
| 0.81692 | 0.46358 | 96.077 |
| 0.65098 | 0.36942 | 96.073 |
| 0.80563 | 0.45717 | 96.078 |

In mean, $\text{Mo}=96.087$.

Palladium.—Atomic weight determined by Joly and Leidié² by means of potassium palladio-chloride, K_2PdCl_6 . In the first series of experiments the salt was dried in vacuo at ordinary temperature. It was then electrolyzed in a solution acidulated with hydrochloric acid, both the palladium and the potassium chloride being weighed. The palladium was dried, ignited in a stream of hydrogen, and cooled in an atmosphere of carbon dioxide. Results as follows:

| Wt. salt. | Wt. Pd . | Wt. KCl . | At. Wt. Pd . | |
|-----------|-------------------|--------------------|---------------------------|-----------------------------|
| | | | From salt : Pd . | $\text{Pd} : 2\text{KCl}$. |
| 1.0255 | 0.3919 | 0.5520 | 105.749 | 105.643 |
| 1.2178 | 0.3937 | 0.5551 | 104.881 | 105.535 |
| 1.2518 | 0.4048 | 0.5687 | 104.923 | 105.916 |

This series was rejected by the authors upon finding that the salt retained water. In one experiment 0.23 per cent. of water was found. Accordingly a second set of determinations was

¹ This JOURNAL, 15, 397, July, 1893. Results calculated with $\text{O}=16$, $\text{Na}=23.05$, and $\text{Cl}=35.45$.

² Compt. rend., 116, 147, 1893. Results calculated with $\text{O}=15.96$, $\text{Cl}=35.37$, $\text{KCl}=74.40$, and $\text{H}=1$.

made in which the palladio-chloride was dried in vacuo at 100°.

| Wt. salt. | Wt. Pd. | Wt. KCl. | At. Wt. Pd. | |
|-----------|---------|----------|-------------|------------|
| | | | Salt : Pd. | Pd : 2KCl. |
| 1.3635 | 0.4422 | 0.6186 | 105.374 | 106.368 |
| 3.0628 | 0.9944 | 1.3929 | 105.545 | 106.229 |
| 1.4845 | 0.4816 | 0.6782 | 105.405 | 105.694 |
| 1.7995 | 0.5838 | 0.8206 | 105.427 | 105.861 |

The mean of the values found from the ratio K_2PdCl_4 : Pd is 105.438. If $O=16$, this becomes $Pd=105.702$. With $O=15.88$ we get 104.910. The KCl values were rejected.

Still another set of determinations was based upon the reduction of the double chloride in a stream of hydrogen, the data being in other respects like the foregoing. Results as follows:

| Wt. salt. | Wt. Pd. | Wt. KCl. | At. Wt. Pd. | |
|-----------|---------|----------|-------------|----------|
| | | | Salt : Pd. | Pd : KCl |
| 2.4481 | 0.7949 | 1.1168 | 105.560 | 105.911 |
| 1.8250 | 0.5930 | 0.8360 | 105.671 | 105.656 |

It is noticeable that these values, in the set K_2PdCl_4 : Pd, run higher than in the electrolytic series. Inasmuch as the latter experiments were made in presence of free hydrochloric acid, it would seem possible that chlorine may have been liberated, preventing complete precipitation of the palladium, and so slightly lowering the apparent atomic weight of the latter. At all events the results obtained are not sharply concordant, and are, therefore, inconclusive.

Barium.—An elaborate memoir upon the atomic weight of barium, by Richards,¹ makes a notable change in the value of that constant. Barium bromide was the compound investigated, and the procedure consisted in titrating its solution with solutions containing known quantities of silver. In many of the experiments the silver bromide thrown down during titration was collected and weighed. From the weights of Ag and of AgBr found, the ratio Ag : Br may be computed as a check on the accuracy of the work.

Full details are given concerning purity of materials, processes, weighings, etc., for which the original memoir must be consulted. The final results are stated in the following columns: First, BaBr, corresponding to 100 parts Ag. Second,

¹ *Proc. Amer. Acad.*, 28, 1. Presented Jan. 11, 1893.

BaBr, corresponding to 174.080 parts AgBr. Third, percentage of Ag in AgBr.

| Exp. | I. | II. | III. |
|-----------------------------|---------|----------------|--------|
| 1..... | 137.746 | 137.783 | 57.460 |
| 2..... | 137.736 | 137.760 | 57.455 |
| 3..... | | 137.723 | |
| 4..... | 137.732 | | |
| 5..... | 137.735 | 137.739 | 57.447 |
| 6..... | 137.748 | 137.748 | 57.445 |
| 7..... | 137.747 | | |
| 8..... | 137.740 | 137.747 | 57.448 |
| 9..... | 137.755 | 137.748 | 57.442 |
| 10..... | 137.738 | 137.752 | 57.451 |
| 11..... | 137.747 | 137.772 | 57.455 |
| 12..... | | 137.726 | |
| 14..... | 137.750 | 137.745 | 57.443 |
| 15..... | 137.756 | 137.754 | 57.445 |
| 16..... | 137.731 | | |
| 17..... | 137.748 | | |
| 18..... | | 137.745 | |
| 19..... | 137.759 | 137.758 | 57.445 |
| Mean, omitting 1 and 2..... | 137.745 | 137.747 | 57.448 |
| | | Stas found.... | 57.445 |

The last column, by its agreement with Stas' measurements, serves to confirm the other two, from which the atomic weight of barium is easily computed. From the ratio Ag_2BaBr_2 , when $\text{Ag}=107.93$ and $\text{Br}=79.955$,

$$\text{Ba}=137.426.$$

From the ratio $2\text{AgBr}:\text{BaBr}_2$,

$$\text{Ba}=137.431.$$

The value 137.43 then must replace the lower value commonly held hitherto. The new results appear to be thoroughly established and unimpeachable.

Thallium.—Lepierre¹ has redetermined the atomic weight of this metal by several distinct methods. First, by the electrolysis of thallous sulphate in presence of an excess of ammonium oxalate, weighing first the sulphate and then the metal obtained. The latter was dried and weighed in an atmosphere of hydrogen. The corrected weights and results are as follows:

| Wt. Tl_2SO_4 . | Wt. Tl_2 . | At. Wt. Tl . ($\text{O}=15.96$). |
|--------------------------------|---------------------|---|
| 1.8935 | 1.5327 | 203.52 |
| 2.7243 | 2.2055 | 203.67 |
| 2.8112 | 2.2759 | 203.69 |

¹ *Bull. Soc. Chim.*, (3) 9, 166, March 20, 1893.

Secondly, a weighed quantity of crystallized thallic oxide was converted by means of sulphurous acid into thalious sulphate, which was then subjected to electrolysis as in the preceding series. The results are subjoined.

| Wt. Tl_2O_3 . | Wt. Tl_2 . | At. Wt. Tl. |
|-------------------------------|---------------------|-------------|
| 3.2216 | 2.8829 | 203.76 |
| 2.5417 | 2.2742 | 203.53 |

In the third series of experiments a definite quantity of thalious salt was fused in a polished silver crucible with ten times its weight of absolutely pure caustic potash. Thallic oxide was thus formed, which was washed with water and alcohol under various precautions, dried at 100° , and finally weighed in the original crucible.

| | | At. Wt. Tl. |
|---|--------------------------------|-------------|
| 3.1012 Tl_2SO_4 gave..... | 2.8056 Tl_2O_3 | 203.57 |
| 2.3478 " " | 2.1239 " | 203.44 |
| 2.7591 TlNO_3 " | 2.3649 " | 203.73 |

Finally, crystallized thallic oxide was reduced in a stream of hydrogen, and the water so formed was collected and weighed.

| Wt. Tl_2O_3 . | Wt. H_2O . | At. Wt. Tl. |
|-------------------------------|----------------------------|-------------|
| 2.7873 | 0.3301 | 203.54 |
| 3.9871 | 0.4716 | 203.82 |
| 4.0213 | 0.4761 | 203.00 |

The mean of the eleven figures given for thallium is 203.57, but stated by the author as 203.62. If $\text{O}=16$ this becomes $\text{Tl}=204.08$; and with $\text{O}=15.88$, $\text{Tl}=202.55$. It will be observed that the values found in the individual experiments vary among themselves through a range of over eight-tenths of a unit, and that, therefore, the final mean result is entitled to little consideration. M. Lepierre is evidently unfamiliar with the determinations of his predecessors; for, quite ignoring the admirable work of Crookes, he speaks of the currently accepted value for Tl as resting without proof upon the calculations of Meyer and Seubert. He also neglects to state whether his weighings were reduced to vacuum standards, and he gives no evidence bearing upon the absolute purity and definiteness of the several compounds weighed. The metallic thallium which served as a starting point for the investigations, seems to have been carefully purified.

The Composition of water by Volume.—The volume ratio be-

tween H and O in water, which controls the atomic weight of oxygen as deduced from its density, has been redetermined by Scott.¹ The report published is only in abstract, but the subjoined values for the ratio, $H_2:O$, are given.

2.0020
2.0024
2.0026
2.0030
2.0022
2.0025
2.0029
2.0023
2.0028
2.0017
2.0022
2.0028

Mean, 2.00245, \pm 0.00007.

Combining this mean with the density ratio, $O:H::15.882:1$,² gives for the atomic weight of oxygen the value 15.862.

Scott gives mean results of several other series of experiments, but only this one in detail. The hydrogen was obtained from palladium hydride, and the oxygen from silver oxide. With only an abstract available, the work done cannot be critically compared with Morley's.

The Density of the Principal Gases.—These data, as determined by Lord Rayleigh,³ having important bearing upon atomic weights, fall properly within the scope of this report. Full details are given as to the apparatus used, and all corrections are applied; such, for instance, as for the difference in volume of the glass globes when filled or exhausted, for the value of gravity at the laboratory in latitude $51^{\circ}47''$, etc., etc. The final results are as follows, with air as unity.

| | |
|--------|---------|
| H..... | 0.06960 |
| N..... | 0.97209 |
| O..... | 1.10535 |

The weights in grams per liter are:

¹ *Proc. Roy. Soc.*, 53, 130. Read March 23, 1893.

² Rayleigh.

³ *Proc. Roy. Soc.*, 53, 134. Received March 4, 1893.

| | |
|-----------|---------|
| H..... | 0.09001 |
| N..... | 1.25718 |
| O..... | 1.42952 |
| Air | 1.29327 |

Two of these constants have also been remeasured by Leduc;¹ who gives the following weights for one liter each:

| | |
|----------|---------|
| Air..... | 1.29315 |
| N | 1.2570 |

Miscellaneous Notes.—Richards and Rogers, in a paper upon the occlusion of gases by metallic oxides,² show that when the oxides of copper, nickel, zinc, and magnesium are prepared by the ignition of the nitrates, they retain appreciable quantities of gaseous impurities, such as nitrogen and oxygen, especially the former. The oxides of cadmium, mercury, lead, and bismuth, similarly prepared, contained no gaseous occlusion, excepting a mere trace in the case of cadmium. This observation reveals a possible serious source of error in several determinations of atomic weight, particularly in the cases of zinc and magnesium. In consequence of this fact, the atomic weight of zinc is now under reinvestigation in the Harvard laboratory, the compounds selected for study being the chloride and bromide.

In the study of the rare earths, rough determinations of atomic weight are of great importance in the identification of material. Commonly they are made by the sulphate method, which is familiar to all chemists. Gibbs,³ however, in a study of these substances, makes use of the oxalates. By ignition, the oxide is left and can be weighed, while the proportion of oxalic acid is easily determinable by titration with permanganate solution. In some cases the oxalates were ignited with weighed quantities of pure sodium tungstate, the increase in weight representing R_2O_3 . From the ratio between R_2O_3 and C_2O_3 , the molecular weight of the oxide is easily calculated, and agrees well with determinations made by the sulphate process.

Hinrichs, in a series of communications published in the *Comptes Rendus*,⁴ attempts to show that Stas' determinations

¹ *Compt. rend.*, 117, 1072.

² *Proc. Amer. Acad.*, 28, 200. Presented May 10, 1893.

³ *Am. Chem. J.*, 15, 546, November, 1893.

⁴ On the $KClO_3$ work, in 115, 1074. On the lead determinations, in 116, 431.

of atomic weights are vitiated by systematic errors, depending upon the quantities of material weighed. According to him the larger the weight of the substance employed the larger the error; and he constructs curves to represent his views graphically. His mathematical procedure, however, his "method of limits," is not clear, and it savors somewhat of assuming Proutian values in advance, and then regarding variations from them as errors for which corrections should be applied. At all events he fails to point out, on the basis of experimental evidence, how the supposed errors were produced, and he does not show that they could have been of sufficient magnitude to account for the divergencies to be explained. If Stas' work is to be set aside, it can be by experimental researches only.

In a third¹ paper the same author gives his mathematical process in some detail, and still later he discusses Dumas' experiments relative to the atomic weight of oxygen,² seeking to show that it is exactly sixteen. Very recently he has also discussed the determinations of the same constant made by Keiser, Cooke and Richards, Morley, and Dittmar and Henderson, reaching the conclusion that the ratio $H:O=1:16$ rigorously.³ He objects especially to the use of averages as fallacious, but does not fully establish the legitimacy of his conclusions.

In another journal⁴ Hinrichs criticizes Richards' researches upon the atomic weight of copper. After showing that several published determinations of the electrolytic ratio between silver and copper agree quite well with the ratio 108 : 63.5, he takes up in particular Richards' analyses of copper sulphate, and points out that a part of the data correspond with the even values $O=16$, $S=32$, and $Cu=63.5$. The other work of Richards he dismisses as erroneous, but neglects to show wherein the errors lie.

In still another paper⁵ Hinrichs proposes to abandon gases like O and H as bases for atomic weight determinations, and to

¹ *Compt. rend.*, 116, 695.

² *Compt. rend.*, 116, 753.

³ *Compt. rend.*, 117, 663.

⁴ *Chem. News*, 68, 171, October, 6, 1893.

⁵ *Compt. rend.*, 117, 1075.

adopt carbon (diamond)=12 as the fundamental standard, on the ground that it can be exactly weighed. Oxygen and calcium are combined with this as substandards, becoming sixteen and forty respectively.

Replies to Hinrichs' criticism of Stas have been published by Spring¹ and by Van der Plaats.² Both writers object to the processes of extrapolation of which Hinrichs makes use, and Van der Plaats shows by tabulation of data that the systematic errors alleged to exist in Stas' experiments are not there. Only fortuitous errors occur, and these are of insignificant magnitude. Furthermore, the ratios determined by Stas are so numerous, so varied, and so concordant in their final results that the presumption in their favor is overwhelming.

In the same paper, indeed, as its main object, Van der Plaats gives the results of a recalculation of Stas' twenty-one ratios by the method of least squares. He does not, however, give his equations nor explain the special form of the method which he used. The results are stated in two tables, one, (A), computed upon the supposition that each ratio is entitled to weight inversely proportional to the square of its mean error; the other, (B), regarding all as of equal weight. O=16 is the base of the system.

| | A | B |
|-----------------------|------------------------|-----------|
| Ag | 107.9244 \pm 0.0136. | 107.9202. |
| Cl | 35.4565 \pm 0.0049. | 35.4516. |
| Br | 79.9548 \pm 0.0101. | 79.9497. |
| I | 126.8494 \pm 0.0166. | 126.8445. |
| S..... | 32.0590 \pm 0.0085. | 32.0576. |
| K | 39.1403 \pm 0.0059. | 39.1414. |
| Na | 23.0443 \pm 0.0043. | 23.0453. |
| Li..... | 7.0235 \pm 0.0051. | 7.0273. |
| Pb | 206.9308 \pm 0.0404. | 206.9089. |
| N | 14.0519 \pm 0.0078. | 14.0421. |
| NH ₄ | 18.0740 \pm 0.0034. | 18.0760. |

Hence H= .. 1.0055 \pm 0.0021. 1.0085.

Another contribution to the Hinrichsian literature is furnished by E. Vogel,³ who criticizes Stas at considerable length. His

¹ *Chem. Ztg.*, 17, 242, February, 22, 1893.

² *Compt. rend.*, 116, 1362.

³ *Bull. Acad. Bruxelles*, (3), 26, 469.

paper is preceded by adverse reports from W. Spring and L. Henry.

In conclusion I submit a table of atomic weights revised to January 1, 1894. Oxygen=16 is taken as the base of the system, but for provisional reasons only. Before long, with improved determinations, it may be practicable to return to the more philosophical $H=1$, when the entire system can be transformed once for all into something like permanent shape. A premature transformation of this kind, however, would only work confusion, without corresponding benefit.

| Name. | Atomic Weight. | Name. | Atomic Weight. |
|-----------------|----------------|-------------------|----------------|
| Aluminum..... | 27. | Neodymium..... | 140.5 |
| Antimony..... | 120. | Nickel..... | 58.7 |
| Arsenic..... | 75. | Nitrogen..... | 14.03 |
| Barium..... | 137.43 | Osmium..... | 190.8 |
| Bismuth..... | 208.9 | Oxygen..... | 16. |
| Boron..... | 11. | Palladium..... | 106.6 |
| Bromine..... | 79.95 | Phosphorus..... | 31. |
| Cadmium..... | 112. | Platinum..... | 195. |
| Caesium..... | 132.9 | Potassium..... | 39.11 |
| Calcium..... | 40. | Praseodymium..... | 143.5 |
| Carbon..... | 12. | Rhodium..... | 103. |
| Cerium..... | 140.2 | Rubidium..... | 85.5 |
| Chlorine..... | 35.45 | Ruthenium..... | 101.6 |
| Chromium..... | 52.1 | Samarium..... | 150. |
| Cobalt..... | 59. | Scandium..... | 44. |
| Columbium..... | 94. | Selenium..... | 79. |
| Copper..... | 63.6 | Silicon..... | 28.4 |
| Erbium..... | 166.3 | Silver..... | 107.92 |
| Fluorine..... | 19. | Sodium..... | 23.05 |
| Gadolinium..... | 156.1 | Strontium..... | 87.6 |
| Gallium..... | 69. | Sulphur..... | 32.06 |
| Germanium..... | 72.3 | Tantalum..... | 182.6 |
| Glucinum..... | 9. | Tellurium..... | 125. |
| Gold..... | 197.3 | Terbium..... | 160. |
| Hydrogen..... | 1.008 | Thallium..... | 204.18 |
| Indium..... | 113.7 | Thorium..... | 232.6 |
| Iodine..... | 126.85 | Thulium..... | 170.7 |
| Iridium..... | 193.1 | Tin..... | 119. |
| Iron..... | 56. | Titanium..... | 48. |
| Lanthanum..... | 138.2 | Tungsten..... | 184. |
| Lead..... | 206.95 | Uranium..... | 239.6 |
| Lithium..... | 7.02 | Vanadium..... | 51.4 |
| Magnesium..... | 24.3 | Ytterbium..... | 173. |
| Manganese..... | 55. | Yttrium..... | 89.1 |
| Mercury..... | 200. | Zinc..... | 65.3 |
| Molybdenum..... | 96. | Zirconium..... | 90.6 |

Discussion.—Dr. Wiley. By our organization we are able to present to American chemists the latest and most accurate numbers for atomic weights. It is a matter for congratulation that this has been accomplished by the American Chemical Society.

UPON THE DETERMINATION OF NITRATES IN POTABLE WATER.

By AUGUSTUS H. GILL.

Received February 19, 1894.

PART II.

(b) THE REDUCTION TO AMMONIA.

AFTER a discussion of the various processes for the determination of nitrates by reduction to ammonia, Tiemann concludes with the following:¹ "On account of the unreliability and chances for error which this principle involves, we strongly advise against its use."² Tables are given, pp. 208 *et. seq.*, in which the results obtained by reduction with sodium amalgam, aluminum, and the zinc-copper couple, vary from plus ten to minus thirty-eight per cent. which sufficiently illustrate the unreliability.

The objections to any method for such reduction are in brief:

1. THE NUMEROUS CORRECTIONS TO BE APPLIED:

- I. For free ammonia.
 - II. For nitrates.
 - III. For materials used.
 - IV. For ammonia carried away by the hydrogen.
2. The liability of reducing the organic matter present in the water to ammonia.
 3. The time required and chances for error in manipulation. To the method proposed by Hazen and Clark,³ they not distilling the reduced liquid before nesslerizing are added two more, *viz.* :
 4. The colors produced by the Nessler reagent are in many cases not the same *tone* as the standards, and are usually read higher than the amount of ammonia actually found by distilla-

¹ "Die chem. und bacteriologische Untersuchung des Wassers," Tiemann und Gaertner Braunschweig 1890, 212.

² "Entschieden davon abzurathen."

³ *J. Anal. Appl. Chem.*, 5, 3.

tion;¹ see Nos. 2, 3, and 20 in the following table.

5. When the reduction is finished the liquid in the Nessler tube is not homogeneous, hence the removal of a portion without mixing—which at the same time occasions a troublesome turbidity—does not represent the amount of ammonia actually present.

All these objections might well be waived did the method yield reliable results; but as is shown in the accompanying tables, it is subject to even greater variations than the phenolsulphonic acid process.

RESULTS OF THE ESTIMATION OF NITRATES IN WELL WATERS BY THE ALUMINUM AND PHENOLSULPHONIC ACID METHODS.
PARTS OF NITROGEN IN 100,000.

| No. | P. S. A. | Aluminum | | Differences | | Nitrates. | Chlorine. |
|------|----------|------------|----------------------|---------------|-----------|-----------|-----------|
| | | direct. | crosswise distilled. | From P. S. A. | Per cent. | | |
| 1.. | 0.4000 | 0.4323 | | +0.0323 | 7 | none | 2.93 |
| 2*. | 1.1500 | { 1.0287 } | | { -0.1213 } | { 10 } | 0.0001 | 2.78 |
| | | { 0.8306 } | 0.7407 | { -0.2194 } | { 23 } | | |
| 3*. | 1.0000 | { 0.8306 } | { 0.7407 } | { -0.1694 } | { 17 } | | 2.22 |
| | | { 0.8235 } | { 0.6995 } | { -0.1765 } | { 17 } | | |
| 4.. | 0.9000 | 0.8235 | | -0.0765 | 8 | | 2.16 |
| 5.. | 0.0090 | 0.0041 | | -0.0049 | 50 | | 0.34 |
| 6.. | 0.0085 | 0.0041 | | -0.0044 | 50 | | 0.29 |
| 7.. | 0.0500 | 0.0625 | | +0.0125 | 40 | | 0.75 |
| 8.. | 0.4500 | { 0.3045 } | | { -0.1455 } | { 33 } | | 0.96 |
| | | { 0.3538 } | | { -0.0962 } | { 20 } | | |
| 9.. | 0.0060 | { 0.0288 } | | { +0.0228 } | { 400 } | none | 0.35 |
| | | { 0.0000 } | | { -0.0060 } | { 100 } | | |
| 10.. | 0.0140 | { 0.0329 } | | { +0.0189 } | { 120 } | | 0.34 |
| | | { 0.0513 } | | { +0.0373 } | { 250 } | | |
| 11.. | 0.4200 | 0.3538 | | -0.0662 | 15 | | 0.91 |
| 12.. | 0.0000 | 0.0000 | | | .. | | 0.66 |
| | | 0.0000 | | | .. | | |
| 13.. | 0.0400 | 0.0411 | | +0.0011 | 2 | | 0.54 |
| 14.. | 0.3250 | 0.2472 | | -0.0778 | 21 | | 1.12 |
| 15.. | 0.7000 | 0.7242 | 0.6172 | +0.0242 | 3 | 0.0001 | 3.40 |
| 16.. | 0.7200 | 0.6748 | | -0.0452 | 5 | 0.0003 | 2.40 |
| 17.. | 0.2500 | 0.2634 | | +0.0134 | 5 | 0.0002 | 2.57 |
| 18.. | 0.3000 | 0.3127 | 0.2469 | +0.0127 | 4 | 0.0005 | 2.42 |
| 19.. | 1.0000 | 1.0287 | | +0.0287 | 3 | 0.0000 | 4.60 |
| 20*. | 1.6000 | { 1.3414 } | 1.1522 | -0.2500 | 15 | 0.0002 | 2.42 |
| | | { 1.4418 } | | | | | |
| | | { 1.3579 } | 1.2345 1.3168 | | | | |

¹ The reason for the difference in tone of the reduced solutions is probably due to the presence of hydroxylamine, as the colors produced can be closely imitated by solutions of this compound. This is unaffected by the excess of alkali, and is with difficulty reduced to ammonia; upon distillation it breaks up into ammonia and nitrogen, thus giving rise to a loss of the latter.



By "crosswise" is meant the comparison of the tubes when looked through diametrically instead of axially as is customary; this was done, as the colors were not the same tone, to see if they could be matched more closely; the "distilled" column indicates the results as obtained by distilling a portion of the reduced liquid in addition to nesslerizing directly, it will be observed that these results are *lower* than those obtained by direct reading.

The method is supposed to be particularly valuable in the presence of relatively large amounts of chlorine; of eleven waters there given having a higher percentage than one part per hundred thousand, *five*, Nos. 1, 15, 17, 18, and 19, are estimated from 3-7 per cent. *higher* and *six*, Nos. 2, 3, 4, 14, 16, and 20, are estimated from 8-20 per cent. *lower* than the results of the phenolsulphonic acid process. Of the remaining waters three are estimated much too high and four as much too low.

Let us consider another table, this time of solutions made to contain definite quantities of nitrate; each letter represents a different and independent observer.

RESULTS OF THE DETERMINATION OF NITRATES IN STANDARD
SOLUTIONS BY THE ALUMINUM AND PHENOL-
SULPHONIC ACID METHODS.

PARTS OF NITROGEN IN 100,000.

| No. | Aluminum. | | Theory. | Phenolsulphonic acid. | | |
|-------|-----------|--------|---------|-----------------------|--------|---------------------|
| | A. | B. | | C. | D. | E. |
| 21 .. | 0.0800 | 0.1080 | 0.0950 | 0.1020 | 0.1000 | |
| 22 .. | 1.2800 | 1.3000 | 1.3500 | | 1.2000 | 1.3000 ¹ |
| 23 .. | 0.0200 | 0.0140 | 0.0160 | 0.0200 | 0.0150 | 0.0180 |
| 24 .. | 0.8000 | 0.9500 | 0.8500 | 0.8530 | 0.9500 | 0.9000 |
| 25 .. | 2.0500 | 2.5000 | 2.2100 | 2.4500 | 2.5000 | 2.5000 ² |
| 26 .. | 0.0400 | 0.0340 | 0.0380 | 0.0380 | | 0.0400 |
| 27 .. | 0.0800 | 0.0660 | 0.0950 | 0.1000 | 0.1000 | 0.0930 |
| 28 .. | 0.4200 | 0.3660 | 0.4250 | 0.4150 | 0.4500 | 0.4000 |
| 29 .. | 0.4100 | 0.4040 | 0.4250 | 0.4500 | 0.4250 | 0.4000 |
| 30 .. | 0.0300 | 0.0460 | 0.0350 | 0.0370 | 0.0270 | 0.0300 |
| 31 .. | 0.0130 | 0.0120 | 0.0140 | 0.0215 | 0.0120 | 0.0150 |
| 32 .. | 0.0130 | 0.0180 | 0.0140 | 0.0270 | 0.0150 | 0.0150 |
| 33 .. | 0.0580 | 0.0640 | 0.0650 | 0.0620 | 0.0600 | 0.0550 |
| 34 .. | 0.0610 | 0.0540 | 0.0650 | 0.0740 | 0.0520 | 0.0550 |
| 35 .. | 0.0830 | 0.0880 | 0.0900 | 0.0900 | 0.0920 | 0.0700 |

¹ A later determination gave 1.3250.

² A later determination gave 2.1300.

| No. | Aluminum. | | Theory. | Phenolsulphonic. | |
|-----------|-----------|-------------|---------|------------------|-------------|
| | Average. | Difference. | | Average. | Difference. |
| 21 | 0.0940 | —0.0010 | 0.0950 | 0.1010 | +0.0060 |
| 22X | 1.2900 | —0.0600 | 1.3500 | 1.2500 | —0.1000 |
| 23 | 0.0170 | +0.0010 | 0.0160 | 0.0176 | +0.0016 |
| 24X | 0.8750 | +0.0250 | 0.8500 | 0.9010 | +0.0510 |
| 25X | 2.2750 | +0.0650 | 2.2100 | 2.4833 | +0.2733 |
| 26 | 0.0370 | —0.0010 | 0.0380 | 0.0390 | +0.0010 |
| 27 | 0.0730 | —0.0220 | 0.0950 | 0.0976 | +0.0026 |
| 28 | 0.3930 | —0.0320 | 0.4250 | 0.4216 | —0.0034 |
| 29 | 0.4070 | —0.0180 | 0.4250 | 0.4250 | 0.0000 |
| 30 | 0.0380 | +0.0030 | 0.0350 | 0.0313 | —0.0037 |
| 31 | 0.0125 | —0.0015 | 0.0140 | 0.0162 | +0.0022 |
| 32 | 0.0155 | +0.0015 | 0.0140 | 0.0190 | +0.0050 |
| 33 | 0.0610 | —0.0040 | 0.0650 | 0.0590 | —0.0060 |
| 34 | 0.0575 | —0.0075 | 0.0650 | 0.0603 | —0.0047 |
| 35 | 0.0855 | —0.0045 | 0.0900 | 0.0840 | —0.0060 |
| | | —0.0915 | | | —0.0238 |
| | | +0.0055 | | | +0.0184 |

Numbers 22, 24, and 25 are very obviously incorrectly estimated by both methods; the aluminum process gave in two of these cases results too high; the phenolsulphonic acid process gave likewise in two cases results too high, probably from errors in reading caused by attempting to estimate too deep colors¹ (over 0.1300 parts nitrogen in 100,000).

Considering the other twelve determinations, the aluminum process gave results too low in nine, with a total of 0.0915 parts of nitrogen or *6.6 per cent. too low*, and too high in three with a total of 0.0055 parts of nitrogen or *0.4 per cent. too high*. The phenolsulphonic acid process gave too low results in five cases with a total of 0.0238 parts of nitrogen or *1.6 per cent. too low*, and too high in six cases with a total of 0.0184 parts of nitrogen or *1.3 per cent. too high*.

From this investigation it is evident that the aluminum method, in addition to being more troublesome to execute, yields results even in the presence of chlorine (two parts in 100,000) decidedly lower than the phenolsulphonic acid method: further than this, it was observed that duplicate determinations made by the former process did not present a satisfactory agreement.

¹ This the usual result.

This conclusion I am aware is in direct variance with the statement of Hazen and Clark,¹ who say, "This process (phenol-sulphonic acid) with proper precautions, gives results usually too low and often much too low."

In addition to the aluminum process, other methods of reduction have been studied: Fricke² states that Förster's—the reduction with metallic iron and caustic potash in presence of alcohol—Schmitt's—the reduction with iron and acetic acid—and Ulsch's,—the reduction by 'ferrum reductum' and sulphuric acid—all yield good results, provided 0.5 gram potassium nitrate be present,³ these are suitable for the valuation of saltpeters and are obviously not sufficiently refined for the purposes of water analysis. The other method of Ulsch⁴ by reduction with iron and sulphuric acid and subsequent measurement of the "deficit of hydrogen" is open to the same objection. One milligram potassium nitrate is equivalent to 1.1 cc. of hydrogen, this corresponds to 1.38 parts nitrogen per 100,000.

Harrow's⁴ method, the reduction to nitrate in presence of α naphthylamine and sulphanilic acid is sensitive to 0.04 parts nitrogen per 100,000, or twenty times less delicate than the phenolsulphonic acid process. In my opinion advancement in the estimation of nitric acid for the purposes of water analysis is to be sought, not in any method of reduction to ammonia or nitrous acid, but rather in the formation of organic nitro bodies of high coloring power and constant composition, and with this the writer is already engaged.

In conclusion, I desire to express my indebtedness to Mrs. Richards, Miss Hyams, and Mr. Tuttle, of the Massachusetts Board of Health staff for assistance in making many of the above determinations.

MASS. INST. OF TECHNOLOGY,
LABORATORY OF SANITARY CHEMISTRY,
FEBRUARY, 1894.

¹ *J. Anal. Appl. Chem.*, 5, 3.

² *Ztschr. für angew. Chemie*, April, 1891. *Analyst* 16, 117.

³ *Ztschr. anal. Chem.*, 20, 175. *Analyst* 16, 134.

⁴ *J. Chem. Soc.*, 1891, *Trans.*, 320.

DETECTION OF SALICYLIC ACID IN FOOD.¹

By K. P. Mc ELROY.

SALICYLIC acid has been known for more than half a century, having been discovered in 1838 by Piria¹ in oxidizing the oil of meadow sweet (*Spiraea ulmaria*). But its commercial importance dates back only to 1874 when Kolbe² succeeded in making a synthesis of it from sodium phenolate and carbonic acid. In 1860, in conjunction with Lautemann, he devised another synthetic process³, but as this method involved the use of metallic sodium the product was expensive. .

After securing the entire success of his second process in 1874, Kolbe turned his attention to finding uses for his product. In that and the succeeding year he published a number of papers on⁴ its use as a food preservative, as did several of his pupils and assistants, etc.⁵ Public attention became attracted to the acid and its use as a preservative spread with great rapidity. In 1877 the French Government⁶ found itself obliged to take official action regarding the use in wine of salicylic acid.

Analytical chemists of course were not slow to recognize the new demand on their skill involved by the use of this substance as an addition to food, and methods for its detection were soon elaborated. The number of these methods has yearly increased and at present a fair sized bibliography of analytical literature relative to salicylic acid might be compiled.

The most useful properties of salicylic acid, analytically speaking are that it is volatile with steam, that it is extracted from acid liquids by ether, chloroform, carbon bisulphide or benzol, that it gives a bright purple color with ferric chloride, a green color with copper acetate, and a rose color when boiled with Millon's solution and that when converted into the methyl ester it gives rise to a characteristic odor of wintergreen. The iron test is the one which is universally used for the final recognition of this substance, the previous separation from the food being made either with one of the solvents above named or by distillation. It is extremely delicate, giving a good reaction with a tenth

¹ Read at the Baltimore Meeting, December 27, 1893.

milligram in twenty-five cc. of liquid. The copper test is not particularly delicate, nor is the methyl ester test, at least as far as I am concerned. This latter test has been brought forward particularly by Dr. Curtman, of St. Louis.⁷ The test with Millon's solution is given by other substances extractable from foods by ether. The iron test is not given by any substance occurring in foods and extracted by ether to my knowledge. Carbolic acid gives the reaction nearest approaching it in color of the common substances, but this substance does not occur in food. Tannic acid, a little of which is sometimes taken up by ether from wines, gives a blackish or greenish color which has a tendency to hide the salicylic color.

In the laboratory of the Department of Agriculture the method which has been most commonly used involves the separation of the salicylic acid by distillation with water vapor. The use of distillation for this purpose, separating salicylic acid from food, I believe was first proposed in an unsigned article⁸ appearing in the *Chemiker Zeitung*, in 1882, presumably from the pen of the editor, G. Krause. It was there stated that the method had been elaborated in the laboratory of that paper. Kolbe used distillation for the analytical separation of salicylic acid in 1880.⁹ In using it in this laboratory on the samples of canned vegetables, the analyses of which are recorded in *Bulletin* 13, part 8, of the Division of Chemistry, United States Department of Agriculture, the contents of the can were pulped in a mortar, water added, together with a little phosphoric acid, the mixture strained through a bag, and the liquid subjected to distillation. The distillate was then collected in small portions and each portion separately tested with iron chloride. Mr. W. D. Bigelow who was associated with me in the analyses of these goods, and who made the greater portion of the tests, found the best strength of ferric chloride to be about five mgms. to the cc. The salicylic acid has a tendency to accumulate in the later portions of the distillate, and where the amount present is small, there will be hardly any test given by the first fractions. In illustration of this the following experiment may be adduced. Twenty-five milligrams of salicylic acid were dissolved in 250 cc. of water containing a little phosphoric acid and the mixture subjected to distillation, the distillate being collected in twenty-five cc. portions and the sali-

cylic acid estimated colorimetrically. The results may be tabulated as follows :

| No. | cc. | Reaction. | Quantity found. |
|------------|-----|-------------------------|-----------------|
| 1 | 25 | Distinct but pale..... | |
| 2 | 25 | Somewhat stronger | |
| 3 | 25 | Still stronger | 0.3 mgm. |
| 4 | 25 | " " | 0.4 " |
| 5 | 25 | Bright | 0.5 " |
| 6 | 25 | " | 0.8 " |
| 7 | 25 | " | 0.9 " |
| 8 | 25 | " | 2.2 mgms. |
| 9 | 15 | " | 3.0 " |
| Total..... | | | 8.1 mgms. |

I will quote in further illustration of this tendency the method for the determination of salicylic acid in wine described by M. Ince. In this method 210 cc. of wine are mixed with ten cc. of dilute sulphuric acid and the mixture subjected to distillation, the distillate being collected in fifty cc. portions. The first portion is thrown away and the acid estimated in the next two colorimetrically. The quantity found is multiplied by eight, it being assumed that one-eighth of the total salicylic acid will come over in those two fractions when using the amounts of liquid specified.

All the samples of canned vegetables were examined in this way using the fresh contents of the cans. Afterwards, for various reasons, I had the whole series gone over again and the extraction done in a different fashion. The residual contents of the cans had in the meantime been dried and ground to a powder capable of going through a hundred mesh sieve. Portions of this powder were made into a paste, or rather a very stiff dough, with dilute sulphuric acid, and the product placed in an ordinary ether extraction apparatus where it was extracted with ether for several hours. When the ether extract was evaporated to dryness and the residue taken up with water and distilled, the distillate gave the salicylic acid reaction with much greater brilliancy than had the original test, and many samples were found to contain the acid which had before given only doubtful tests or none at all in some cases. The cause of this difference was no doubt the imperfect extraction in the first method of separation, which practically gave only the salicylic acid present in the juice, while

the later method gave that existing in the solid portions as well. Many reactions were quite faint, so much so as to raise the question of the purpose of the addition of such minute quantities of salicylic acid. The smallness of these quantities was probably due, however, to a cause first pointed out by Kolbe⁹ in 1880. Kolbe found that salicylic acid completely disappeared from wine and from water preserved in casks, while in similar samples preserved in glass this disappearance did not take place. Four months' standing, in some cases, were sufficient to cause this disappearance. As an experiment, he placed thoroughly washed cubes of different woods in glass flasks in contact with different solutions of salicylic acid and found that they caused a complete disappearance of the acid after various periods of time, while control samples in which no wood was placed retained their full content of salicylic acid. From the results of this work he drew the inference that woody tissue not only removed the salicylic acid from solution but caused its total destruction in some way, since he could not recover it from the cubes of woods used in the experiments just cited. The woody tissue of the canned vegetables may have caused an action similar to this.

We also use the ordinary "shaking out" method in the Department laboratory to some extent for such goods as beers and wines. The beer or wine is extracted with about half its volume of ether and the extract evaporated to dryness, and the residue taken up with warm water. The resultant solution is tested in the usual way with iron chloride. Between the two processes of separating the salicylic acid, distillation or shaking out with ether, I do not believe there is much choice, though the former is cheaper and more expeditious. The increased purity and sharpness of the reaction given by the distillate as compared with that given by the residue from the ether extract about counterbalance the fact that only a fraction of the salicylic acid appears in the distillate. Objections against the distillation process were raised in 1889 by certain Dutch chemists,¹⁰ on the ground that in the process of fermentation certain "phenol-like bodies" were sometimes formed which interfered with the reaction. "Phenol-like bodies" would interfere not only with the distillation separation but with any other with which I am

acquainted, since phenol is taken up by immiscible solvents from acid solutions precisely as is salicylic acid.

This year three chemists,¹ writing for different German brewing papers, have claimed that in what is called "color" or "caramel" malt a substance exists which gives all the ordinary salicylic acid reactions. The substance is said to exist in many malt extracts rich in isomaltose. J. Brand isolated the substance from color malt and describes all its reactions as being analogous to those of salicylic acid with the single exception of that with Millon's reagent, with which the new substance gave no reaction. I procured a set of color and caramel malts from the World's Fair and tried to obtain a salicylic acid reaction from them, but could not do so. At my request Mr. Bigelow, who not long ago examined a large number of the beers exhibited at the World's Fair, tried a large number of them with Millon's reagent, using it side by side with the iron solution. He reported to me that the Millon's reagent gave salicylic acid in all the samples, irrespective of the reaction upon the ferric chloride. The latter gave salicylic acid in comparatively few. It is only just to say, however, that where ferric chloride indicated the presence of salicylic acid, the reaction given by Millon's reagent was much brighter than where this was not the case.

¹ Piria. Recherches sur la sâlicine et les produits qui en dârivent. *Ann. de chim. et de phys.*, 1838, 69, 281.

² Kolbe, H. Vorläufige Mittheilung. *J. prakt. Chem.*, 1873-4, 8, 41. Synthese der Paraoxybenzoësäure, *ibid*, 336. Ueber eine neue Darstellungsmethode und einige bemerkenswerthe Eigenschaften der Salicylsäure, *ibid*, 1874, 10, 89.

³ Kolbe, H. and E. Lautemann. Ueber die Constitution und Basicität der Salicylsäure. *Liebig's Annalen*, 1860, 115, 201.

⁴ Kolbe, H. Weitere Mittheilungen über die Wirkungen der Salicylsäure. *J. prakt. Chem.*, 1875, 11, 9; Darstellung chemisch reiner Paraoxybenzoësäure durch Umwandlung der Salicylsäure, *ibid*, 24; Weitere Mittheilung über die Wirkung der Salicylsäure, *ibid*, 213; Ueber die chemische Natur der Salicylsäure, *ibid*, 1875, 12, 151; Abweisung nicht begründeter Urtheile von Halbchemikern über die antiseptischen Eigenschaften der Salicylsäure, *ibid*, 161; Die chemische Natur der Salicylsäure, *ibid*, 151; Chemische Winke für praktische Verwendungen der Salicylsäure, *ibid*, 1876, 13, 106.

Kolbe, H. and E. von Meyer, Versuche über die gâhrungshemmende

Wirkung der Salicylsäure und anderer aromatischer Säuren. *J. prakt. Chem.*, 1875, 12, 133; Ueber die antiseptischen Wirkungen der Salicylsäure und Benzoëssäure in Bierwürze und Harn, *ibid*, 178.

⁵ Fontheimer, Karl. Ueber die Wirkung der Salicylsäure als Arzneimittel. *J. prakt. Chem.*, 1875, 11, 211.

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Neubauer, C. Ueber die Gährungshemmende Wirkung der Salicylsäure. *J. prakt. Chem.*, 1875, 11, 1 and 354, and 12, 331.

Schaer, Ed. Ueber die Veränderung der Eigenschaften der Fermente durch Salicylsäure und einige andere antiseptische Mittel. *J. prakt. Chem.*, 1875, 12, 123.

Wagner, W. Praktische Beobachtungen über die Wirkungen der Salicylsäure. *J. prakt. Chem.*, 1875, 11, 57.

Zürn. Die Salicylsäure in der Veterinärpraxis. *J. prakt. Chem.*, 1875, 11, 215.

⁶ Fauvel, Bergeron and Bussy (reporter). Emploi de l'acide salicylique comme agent de conservation des vins. Rapport sur une demande d'avis adresse par la chambre de commerce de Paris. Recueil des travaux du comité consultatif d'hygiene 1877, 7, 346.

⁷ Curtman, C. O. Nachweis der Salicylsäure durch Synthese des Gaultheriaöls. *Pharm. Rundschau*, 1885, 3, 155; *abs. Chem. Ztg.*, 1885, 9, 1504.

⁸ Anonymous (G. Krause?). Nachweis von der Salicylsäure in Nahrungsmitteln. *Chemiker Ztg.*, 1882, 6, 619.

⁹ Kolbe, H. Zerstörende Wirkung des Holzsubstanz auf Salicylsäure. *J. prakt. Chem.*, 1880, 21, 443 and 22, 112.

¹⁰ Horn, G. A. [Detection of Salicylic Acid in Beer.] *Pharm. Weekblad* (1888?), Nos. 7 and 8; *Apoth. Ztg.*, No. 56; *Ztschr. Nahr. Hyg.*, 2, 150; *Chem. Centrbl.*, 1888, 1425.

¹¹ Erich, E. Ueber die Salicylsäurereaction der Caramelfarbmälze. *Bierbrauer*, 1893, 24, 465; *abs. Chem. Ztg. Rep.*, 1893, 17, 211.

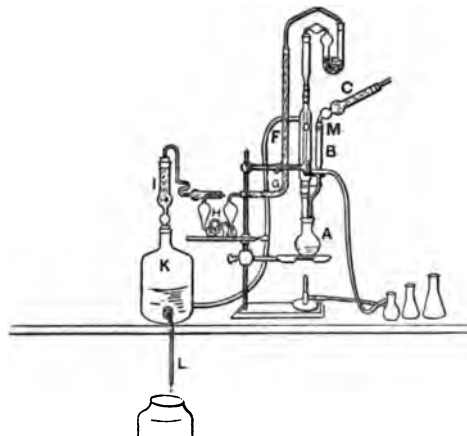
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Brand, J. Die scheinbare Salicylsäurereaction bedingenden Körper der Caramelmälze. *Ztschr. ges Brauwesen*, 1893, 16, 303; *abs. Chem. Ztg. Rep.*, 1893, 17, 242.

A CONVENIENT FORM OF APPARATUS FOR THE ESTIMATION OF CARBONIC ACID.

BY ROBERT H. FORBES.

THE form of apparatus for the estimation of carbonic acid devised by the writer and shown herewith, has been fully tested in our laboratories and found to be accurate, cheap, compact, easily portable, and applicable both to the estimation of carbonic acid in carbonates and to that of carbon in iron by the



wet combustion with chromic and sulphuric acids. C is a tube, filled with solid potash, guarding the apparatus from the carbonic acid of the air. The small drop funnel B carries acid to the decomposing flask A. The small condenser D returns most of the water vapor, and the hydrochloric acid to the decomposing flask. The

small U tube E, containing a solution of silver sulphate in sulphuric acid, stops hydrogen sulphide and traces of hydrochloric acid. The drying tube F G, of one-half inch combustion tubing, and filled with calcium chloride, finally dries the carbonic acid gas before its absorption at H. The calcium chloride tube I guards the bulbs from moisture, and the aspirating bottle is discharged by the movable tube L.

When used for carbonates, a fifty cc. wide mouthed flask is best, but this must be replaced by a 250 cc. Erlenmeyer flask when making a wet combustion of carbon.

In practice it is found best, after the evolution flask is in position, to turn down the outlet tube L, and regulate the flow en-

tirely from the stop-cock B. Hydrochloric acid rarely gets beyond the condenser, and the downward pitch of the drying tube F G hastens the passage of the carbonic acid gas. The whole apparatus occupies less than two square feet of desk room.

CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, AUGUST 25, 1893.

THE SPECIFIC GRAVITIES OF SOME GEM STONES.¹

BY A. LIVERSIDGE, M.A., F.R.S., PROFESSOR OF CHEMISTRY, UNIVERSITY OF SYDNEY.

THE following tables contain the specific gravities of some gem stones which were all in the cut and polished condition except in the cases specified. As the specimens were sufficiently free from flaws and mechanical impurities to be cut and polished for jewelry, the specific gravities can be taken as those of typically pure minerals and the results should be more satisfactory than those obtained from ordinary cabinet specimens, unless it can be shown that the specific gravity is altered by the pressure and other treatment they have received during the process of cutting and polishing.

The specific gravities were taken with special care on an Oertling's best chemical balance by direct weighing, *i. e.*, by suspending the specimen in a very small and light metal stirrup in distilled water. A specific gravity bottle was found, as is well known, to give less accurate results.

The temperature at the time of the determination is given in all cases and the results are corrected to 4° C. according to Rossetti's determinations of the density of water.

In the last column are given the extremes of specific gravity as given by F. W. Clarke in his Constants of Nature.

The numbers refer to those in my catalogue of specimens and added in case of future reference.

¹ Read before the World's Congress of Chemists, August 23, 1893.

| No. of Spec. | Name. | Locality. | Temperature. | Weight. | Sp. Gr. | Corrected to +4° C. |
|--------------|--|------------------|--------------|---------|---------|---------------------|
| 63 | Beryl Beryllium silico-aluminate..... | | 20° C. | 0.1260 | 2.6359 | 2.6312 |
| 62 | " (five small stones) pale green..... | | " | 0.5640 | 2.7865 | 2.7816 |
| 43 | " " " " " " " " " " " " | | 21.5° C. | 0.1225 | 2.7282 | 2.7282 |
| 39 | " " " " " " " " " " " " | | " | 1.0108 | 2.6886 | 2.6773 |
| | F. W. Clarke gives a range from 2.650 to 2.725..... | | | | | |
| | CHRYSOBERYL Beryllium aluminate..... | Ceylon. | 19° C. | 0.3615 | 3.4330 | 3.4277 |
| 27 | Cymophane or cat's eye (three small stones)..... | " | 21° C. | 1.8665 | 3.7147 | 3.7074 |
| 14 | " " " " " " " " " " " " | " | " | 2.1986 | 2.9299 | 2.9241 |
| 15 | " " " " " " " " " " " " | " | 19° C. | 0.5193 | 3.6882 | 3.6825 |
| 22 | " " " " " " " " " " " " | " | " | 0.6445 | 3.7040 | 3.6982 |
| 24 | " " " " " " (four small stones)..... | " | " | | | |
| | F. W. Clarke gives a range from 3.597 to 3.860..... | | | | | |
| | CHRYSOLEITE. Magnesium iron silicate..... | | 21.5° C. | 0.2186 | 3.3839 | 3.3772 |
| 45 | CORUNDUM. Alumina..... | New South Wales. | 21.5° C. | 1.5350 | 3.9974 | 3.9895 |
| 33 | Adamantine spar..... | " | 18.5° C. | 0.5884 | 3.7382 | 3.7331 |
| 19 | Barklyite (four uncut stones)..... | Ceylon. | 21° C. | 0.3557 | 4.0160 | 4.0081 |
| 20 | " " " " " " " " " " " " | " | " | 0.2644 | 4.0060 | 3.9981 |
| 40 | " (six small stones)..... | " | 21.5° C. | 0.3590 | 3.9977 | 3.9898 |
| 15 | " star..... | " | 19° C. | 0.4230 | 3.9586 | 3.9525 |
| 13 | " " " " " " " " " " " " | " | 21° C. | 0.1876 | 4.0960 | 4.0880 |
| 10 | " " " " " " " " " " " " | " | 20° C. | 3.7392 | 3.9920 | 3.9850 |
| | F. W. Clarke gives a range from 3.511 to 3.994 for star ruby.... | | | | | |
| | Sapphirine, pale blue..... | New South Wales. | 19° C. | 0.3130 | 3.8832 | 3.8822 |
| 7 | " royal blue..... | " | 18° C. | 0.1398 | 4.1117 | 4.1061 |
| 10 | " " " " " " " " " " " " | " | 19° C. | 0.6486 | 3.9243 | 3.9243 |
| 17 | " " " " " " " " " " " " | " | 21.5° C. | 0.2330 | 3.9827 | 3.9751 |
| 38 | " " " " " " " " " " " " | " | " | 0.4770 | 4.0219 | 4.0140 |
| 42 | " " " " " " " " " " " " | Ceylon. | 18.5° C. | 0.5950 | 4.1124 | 4.1068 |
| 15 | " (four) dark colored..... | " | 20° C. | 2.5380 | 3.9333 | 3.9284 |
| 5 | " " " " " " " " " " " " | " | 19° C. | 0.8713 | 3.9730 | 3.9663 |
| 1 | pale blue..... | " | " | | | |
| 6 | " " " " " " " " " " " " | " | 20° C. | | | |

| | | | Temperature. | Weight. | Sp. Gr. | Corrected to 4° C. |
|-----|---|-------------------|--------------|---------|---------|--------------------|
| 7 | Sapphire | | 20° C. | 1.2660 | 3.9476 | 3.9407 |
| 8 | " | | " | 0.8220 | 4.0039 | 3.9969 |
| 1 | " yellow; large "Oriental topaz" | | " | 5.0802 | 4.0089 | 4.0019 |
| 16 | " | | 19° C. | 0.5056 | 3.9164 | 3.9103 |
| 2 | " star..... | | " | 1.1352 | 3.9943 | 3.9981 |
| 9 | " blue grey star | | 20° C. | 4.4812 | 3.9914 | 3.9844 |
| 11 | " star..... | | 21° C. | 2.8314 | 3.9969 | 3.9890 |
| 12 | " | | " | 0.2973 | 4.0284 | 4.0205 |
| 29 | " | | 19° C. | 1.2374 | 3.9967 | 3.9905 |
| 23 | F. W. Clarke gives a range from 3.562 to 4.022. | | | | | |
| 25 | Green sapphire or oriental emerald..... | Ceylon. | | | | |
| 23 | " " (two small stones)..... | " | 19° C. | 0.2872 | 4.1146 | 4.1082 |
| 25 | " | " | " | 0.9674 | 4.0041 | 3.9979 |
| 25 | " | Cudgong, N. S. W. | 18.5° C. | 0.5996 | 4.0733 | 4.0678 |
| 2 | " yellow..... | New South Wales. | 20° C. | 1.5972 | 3.9738 | 3.9668 |
| 3 | " pale green..... | " | " | 2.9772 | 4.0000 | 3.9930 |
| 61 | DIAMOND..... | | | | | |
| | Diamond, dark uncut octohedron..... | Bingera, N. S. W. | 20° C. | 0.2920 | 3.4762 | 3.4701 |
| | " five dark colored, uncut..... | " | 18.5° C. | 1.3220 | 3.5633 | 3.5585 |
| | " six light "..... | | " | 2.2790 | 3.5778 | 3.5730 |
| | F. W. Clarke gives a range from 3.334 to 3.550..... | | | | | |
| 16 | FELDSPAR. Potassium aluminum silicate..... | | | | | |
| 17 | " | Ceylon. | 21° C. | 0.7370 | 2.9877 | 2.9826 |
| 18 | " | " | " | 0.3534 | 2.9833 | 2.9782 |
| | " | " | " | 0.2288 | 2.9833 | 2.9772 |
| | F. W. Clarke gives a range from 2.5702 to 2.9950..... | | | | | |
| 44 | GARNETS..... | | | | | |
| 49a | Garnet, almandine. Iron aluminum silicate..... | | 21.5° C. | 0.1510 | 4.0266 | 4.0187 |
| 59 | " two specimens "..... | | " | 0.1248 | 4.0519 | 4.0439 |
| 37 | " three "..... | | 20° C. | 1.3708 | 4.0088 | 3.9988 |
| 41 | " two "..... | | 21.5° C. | 0.3038 | 4.1369 | 4.1308 |
| | " two " very dark..... | | " | 0.2558 | 4.0862 | 4.0792 |

| No. of Spec. | Name. | Locality. | Temperature. | Weight. | Sp. Gr. | Corrected to 4° C. |
|--------------|--|-----------------------|--------------|---------|---------|--------------------|
| 60 | Garnet..... | | 20° C. | 1.3768 | 4.0537 | 4.0566 |
| 64 | " three specimens..... | | " | 0.3280 | 4.1000 | 4.0928 |
| 65 | " two " very dark..... | | " | 0.2748 | 3.9458 | 3.9389 |
| 37a | " " " "..... | | 21.5° C. | 0.5714 | 4.2515 | 4.2431 |
| 53 | " cinnamon stone. Calcium aluminum silicate..... | | 20° C. | 0.4566 | 3.6448 | 3.6384 |
| 28 | " " " "..... | | 19° C. | 0.4039 | 3.6420 | 3.6363 |
| 54 | " " " less full of air bubbles..... | | 20° C. | 0.5157 | 3.7342 | 3.7276 |
| | F. W. Clarke gives a range for almandine of from 3.900 to 4.236.
" " " cinnamon stone " 3.252 to 3.609. | | | | | |
| 50 | LAPIS LAZULI, four pieces cut and polished for stud links..... | | 21.5° C. | 1.3560 | 2.7684 | 2.7629 |
| | PEARLS. Calcium carbonate..... | | | | | |
| 46 | Pearl, three specimens..... | Ceylon. | 21.5° C. | 0.2841 | 2.7291 | 2.7237 |
| 47 | " " " very irregular..... | Torres Straits. | " | 1.1422 | 2.6837 | 2.6784 |
| 48 | " " " "..... | " " | " | 0.4510 | 2.6845 | 2.6792 |
| | QUARTZ. Silica..... | | | | | |
| 56 | Rock crystal..... | | 20° C. | 0.2255 | 2.6877 | 2.6830 |
| | F. W. Clarke gives a range from 2.61 to 2.6507 at 0° C..... | | | | | |
| 57 | Amethyst..... | | | | | |
| | " purchased at..... | | | | | |
| | F. W. Clarke gives a range from 2.659 to 2.744..... | | | | | |
| 26 | Rose Quartz, two specimens..... | Oberstein | 20° C. | 0.4756 | 2.6481 | 2.6434 |
| | F. W. Clarke gives a range from 2.651 to 2.658..... | | 18° C. | 5.2408 | 2.6565 | 2.6529 |
| | Calngorm, purchased at..... | Ceylon. | 19° C. | 1.1598 | 2.6674 | 2.6632 |
| | " " " "..... | | | | | |
| | " " " "..... | Oberstein. | 18° C. | 22.4670 | 2.6535 | 2.6519 |
| | " " " "..... | " | " | 15.6990 | 2.6533 | 2.6517 |
| | " " " "..... | " | " | 13.3554 | 2.6567 | 2.6531 |
| | " " " "..... | " | " | 3.9084 | 2.6567 | 2.6531 |
| | F. W. Clarke gives a range from 2.651 to 2.658 (smoky)..... | | | | | |
| 8 | Fibrous Quartz, "Cat's eye,"..... | N. S. W., West. Dist. | 18.5° C. | 0.2636 | 2.6703 | 2.6667 |
| 34 | Opal. Hydrous silica, two specimens..... | New South Wales. | 19° C. | 0.1150 | 2.0105 | 2.0074 |
| 35 | " " " "..... | " | 21.5° C. | 0.1858 | 2.0690 | 2.0649 |
| 6 | " " " flawed..... | " | 19° C. | 0.3616 | 2.0769 | 2.0746 |

| No. of Spec. | Name. | Locality. | Temperature. | Weight. | Sp. Gr. | Corrected to 4° C. |
|--------------|---|------------------|--------------|---------|---------|--------------------|
| 8 | SPINEL. Magnesium aluminate..... | | | | | |
| 35 | Spinel, dark blue | Ceylon. | 18° C. | 0.3906 | 3.6392 | 3.6343 |
| 36 | " puce..... | " | 21.5° C. | 0.3468 | 3.5900 | 3.5829 |
| | " dark puce..... | " | " | 0.1616 | 3.5831 | 3.5761 |
| | F. W. Clarke gives a range from 3.48 to 3.77..... | | | | | |
| | TOPAZ. Aluminum silico-fluoride..... | | | | | |
| 1 | Topaz, colorless..... | New South Wales. | 19° C. | 1.5213 | 3.5602 | 3.5547 |
| 18 | " | " | 18° C. | 11.6010 | 3.5909 | 3.5461 |
| 58 | " | " | 20° C. | 0.6334 | 3.5110 | 3.5048 |
| 32 | " two white..... | Ceylon. | 21.5° C. | 2.0280 | 3.5717 | 3.5647 |
| 51 | " | " | 20° C. | 0.4282 | 3.5330 | 3.5268 |
| 31 | " yellow Brazilian..... | Brazil. | 21.5° C. | 0.3162 | 3.5728 | 3.5658 |
| 30 | " pink " burnt..... | " | 19° C. | 1.0845 | 3.5406 | 3.5372 |
| 52 | " | " | 20° C. | 0.8920 | 3.5257 | 3.5195 |
| 13 | " | " | 19° C. | 0.4413 | 3.4676 | 3.4622 |
| 55 | " | " | 20° C. | 0.6695 | 3.5991 | 3.5668 |
| | F. W. Clarke gives a range from 3.439 to 3.597..... | | | | | |
| 12 | TOURMALINE. Aluminum boro-silicate..... | | | | | |
| | " brown colored specimen..... | Ceylon. | 19° C. | 0.4835 | 3.0087 | 3.0040 |
| | F. W. Clarke gives a range from 2.997 to 3.243 and from 3.035 to 3.068 for brown tourmalines..... | | | | | |
| 5 | Tourquoise. Hydrous aluminum phosphate..... | | | | | |
| | F. W. Clarke gives a range from 2.456 to 2.651..... | Sinal. | 19° C. | 0.3440 | 2.7388 | 2.7345 |
| | ZIRCONS. Zirconium silicate..... | | | | | |
| 4 | Zircon, red | New South Wales. | 19° C. | 0.4026 | 4.4783 | 4.4714 |
| 9 | " | " | 18° C. | 0.3118 | 4.7822 | 4.7757 |
| 10 | " cut and polished..... | " | 18.5° C. | 1.8445 | 4.7191 | 4.7127 |
| 14 | " pale green..... | Ceylon. | 19° C. | 0.4160 | 4.5921 | 4.4951 |
| | F. W. Clarke gives a range from 4.047 to 4.709 at 21° C..... | | | | | |

NOTES ON THE GRANDEAU METHOD FOR THE DETERMINATION OF HUMUS IN SOILS.

BY HARRY SNYDER.

Received January 18, 1894.

THE Grandeau method for the determination of humus in soils, without some modifications, is open to serious objections: (1) It is difficult to obtain a complete extraction of the humus materials with ammonia, as ordinarily carried on, especially when the soil is very fine and of a clayey nature. (2) The filtration is frequently so slow that a week is sometimes required before the filtrate becomes clear. (3) During all of this time the laboratory is so filled with fumes of ammonia as to seriously interfere with other lines of work.

To say the least, the present method is slow, cumbersome, and gives unsatisfactory results with many kinds of soils. The author has had in use during the past year, a few simple modifications, that have given good results.

After treatment with the dilute acid, the soil is transferred to either a glass-stoppered bottle, or a glass-stoppered Erlenmeyer flask of 100 cc. capacity, using fifty or sixty cc. of the dilute ammonia solution for that purpose. The contents of the bottle or flask are then well shaken at frequent intervals, and then allowed to settle. After settling, the dark colored solution is decanted into a filter, a fresh fifty cc. portion of the dilute ammonia solution is then added to the flask, and the same treatment repeated. It usually requires three or four such treatments before the filtrate becomes clear; the contents of the flask are then brought on to the filter, and require but little farther washing in the usual way before this part of the operation is completed. While the second, third, and fourth treatment with the ammonia is being carried on, the first portion of the filtrate can be evaporated on the water bath, and thus save time when that part of the operation is reached. The most progress can be made by making as large a number of determinations at one time as a person can conveniently take care of, so as not to unnecessarily hurry the operations, nor lose too much time in

making the humus determinations of the soil. A separate room for such work is a great convenience.

The results obtained by this method of treatment are much higher than those obtained when working in the usual way. This is to be expected, inasmuch as more complete extraction of the humus materials are obtained by using the glass-stoppered flasks. Duplicate results with the ordinary Grandeau method are far from being concordant, while with the glass-stoppered flasks reasonably concordant results are secured.

The Grandeau method for the determination of humus, when properly carried out, is capable of giving results that are of practical agricultural value. The examination of a few typical cases out of over a hundred samples of soil examined in the laboratory of the Minnesota Experiment Station, during the past two years, will show that the results obtained by the modified Grandeau method are well worth all of the time and labor that has been spent. Before examining the results, two points are to be noted:

First. There are many other organic compounds of equal agricultural value that are not included in the ammonia extract. Take for example any of the soils that show from ten to fifteen per cent. of volatile matter. The combined water, carbon dioxide, and humus, as well as volatile mineral matters account for sixty to seventy-five per cent., only, of the volatile material, leaving twenty-five per cent. of the volatile organic materials not accounted for. These organic materials, may, in time, become soluble in the ammonia solution, and finally be classed as humus materials. The Grandeau method gives us no idea of the extent to which these organic substances may be present in the soil.

Second. Along with the humus soluble materials are variable amounts of phosphoric acid. A careful study of the total phosphates, humus and phosphates soluble with the humus fails to indicate any chemical combination between the humus and the ammonia soluble phosphates. At this point another serious difficulty presents itself: Some soils which are rich in both phosphoric acid and lime, will give up some of their phosphoric acid to the dilute hydrochloric acid solution

that is first used to remove the lime. This appears to be quite prominent with some of the native soils that are particularly rich in total phosphates, humus, and lime. The analyses of many of these soils showed that the phosphates soluble in the dilute ammonia, and supposed to be in combination with the humus as available phosphoric acid, was less, in many soils, even when the humus was found to be high, than in other soils that were known to be far less fertile. A repetition of the work showed that the dilute hydrochloric acid used in removing the high percentages of lime, also removed a large portion of the phosphates that would have been soluble in the ammonia. Is not this phosphoric acid equally as valuable, agriculturally, as that soluble in the dilute ammonia? Qualitative tests can easily be made of the hydrochloric acid washings, to determine the presence or absence of phosphates.

In the native soils there is quite a close relation between the humus, as determined by the modified method, and the total nitrogen. The table given, shows the amounts of humus and nitrogen, as well as the ratio between the two, in a number of native soils, and soils that have been cultivated for various periods without the use of fertilizers. The volatile matter given includes both the total organic matter and the combined water, the carbon dioxide, hygroscopic moisture, etc., having been separately determined and subtracted from the total volatile matter.

RATIO OF NITROGEN TO HUMUS.

| Description of soil. | No. of soil. | Total volatile per cent. | Humus per cent. | Total nitrogen per cent. | Ratio. |
|----------------------------|--------------|--------------------------|-----------------|--------------------------|--------|
| Virgin soil | 203 | 15.55 | 5.34 | 0.38 | 13.97 |
| 10 years cultivation | 298 | 5.58 | 3.02 | 0.25 | 12.10 |
| Virgin soil | 202 | 8.10 | 5.16 | 0.41 | 12.60 |
| 10 years cultivation | 236 | 5.48 | 2.87 | 0.21 | 13.60 |
| Virgin soil | 272 | 14.29 | 5.16 | 0.39 | 13.23 |
| 8 years cultivation | 309 | 9.67 | 3.16 | 0.25 | 12.60 |
| 6 " " | 224 | 10.90 | 5.12 | 0.38 | 13.20 |
| Native prairie | 224 | 12.05 | 4.04 | 0.37 | 10.91 |
| 10 years cultivation | 312 | 8.15 | 2.60 | 0.22 | 11.80 |
| 6 " " | 249 | 11.50 | 4.92 | 0.41 | 12.00 |
| 10 " " | 208 | 7.13 | 2.68 | 0.24 | 11.18 |
| 8 " " | 210 | 4.04 | 3.02 | 0.24 | 12.60 |

| Description of soil. | | No. of
soil. | Total
volatile
per cent. | Humus
per cent. | Total
nitrogen
per cent. | Ratio. |
|---------------------------|--|-----------------|--------------------------------|--------------------|--------------------------------|--------|
| 10 years cultivation..... | | 257 | 8.68 | 2.48 | 0.19 | 13.10 |
| 15 " " | | 234 | 6.47 | 2.48 | 0.20 | 12.40 |
| 3 " " | | 220 | 12.40 | 4.17 | 0.37 | 11.28 |
| 3 " " | | 218 | 6.56 | 3.73 | 0.30 | 12.43 |
| 20 " " | | 261 | 8.73 | 2.84 | 0.26 | 11.31 |
| 30 " " | | 279 | 8.31 | 1.80 | 0.16 | 11.25 |
| 40 " " | | 242 | 7.04 | 2.41 | 0.21 | 11.50 |
| 6 " " | | 222 | 10.33 | 3.42 | 0.28 | 13.00 |
| 18 " " | | 269 | 9.44 | 3.91 | 0.34 | 11.50 |
| 25 " " | | 290 | 3.54 | 2.27 | 0.17 | 13.35 |
| 6 " " | | 273 | 8.13 | 4.18 | 0.37 | 11.33 |
| 18 " " | | 249 | 7.94 | 2.04 | 0.17 | 12.00 |

There is, on the average, about twelve parts of humus in the soil, as determined by the method given, to every one part of nitrogen. In the long cultivated soils which have received no fertilizers, the nitrogen and the humus have decreased in about the same ratio. The losses and relationships are not in strict accordance to a mathematical ratio, but it is sufficient to show that there is a relationship between the humus and the nitrogen in a virgin soil, and in soils which have been cultivated without the use of fertilizers.

UNIVERSITY OF MINNESOTA,
LABORATORY OF THE
COLLEGE OF AGRICULTURE.

NOTES.

The Opening of the Kent Chemical Laboratory of the University of Chicago.—In response to invitations sent out by the authorities of the University of Chicago to the chemists throughout the country to be present at the formal opening exercises of the Kent Chemical Laboratory, January 1 and 2, 1894, about fifty chemists assembled in the auditorium of the laboratory, at two o'clock P. M., January 1. It was proposed that the first meeting should be a conference of teachers of chemistry. President Harper delivered a brief address of welcome and closed by saying that Prof. Remsen had consented to act as chairman of the conference—Prof. Remsen then took the chair and after a few introductory remarks introduced Prof. Paul C. Freer, of the

University of Michigan, who had been invited to open the discussion by reading a paper on, "The Teaching of Chemistry in Secondary Schools and Colleges." After Prof. Freer's paper which was very suggestive, a general and spirited discussion ensued which was alike enjoyable and helpful to all present.

At six o'clock dinner was served at the hotel Windermere to the visiting chemists who were the guests of the University. The dinner was elegant in every particular. No "after dinner speeches" were made but during the progress of the courses president Harper announced that it had been proposed that the chemists present, organize a chemical society of some sort and as he knew very little about it he would call on Prof. Nef to state the nature of the proposed plan—Prof. Nef said that the idea was to organize a society of teachers of chemistry to meet at least once a year to discuss methods of teaching chemistry. He invited discussion and after remarks by a few chemists, a motion was made and carried, referring the whole subject to a committee, to be appointed by the chairman, to report to a meeting to be held the next morning at nine o'clock, in the auditorium of the Kent Laboratory. President Harper asked Prof. Remsen to appoint the committee, and he named: Profs. A. B. Prescott, J. U. Nef, P. S. Baker, W. W. Daniells, and A. V. Young.

Immediately after the dinner the chemists returned to the auditorium of the laboratory where at eight o'clock the dedicatory exercises began. President Harper with Mr. Sidney A. Kent headed the procession, followed by Prof. Remsen, Rev. Dr. Northrup, Prof. Nef, the visiting chemists and the faculty of the University. The visiting chemists occupied front seats in the audience while the speakers, Mr. Kent, and the faculty sat on the platform. The dedicatory prayer was delivered by Dr. Northrup, of the University of Chicago. President Harper then delivered a short address in which he read the letter of donation from Mr. Kent. It was as follows:

"Mr. William R. Harper, president of the University of Chicago—My Dear Sir: I hereby give this building, fully furnished and completely equipped, to the University of Chicago as a chemical laboratory for the use of this and future generations. Trusting that the standard of educa-

tion will be such as to command the respect not only of this country but of the civilized world.

Very Truly Yours,

"Chicago, Jan. 1, 1894."

S. A. KENT.

Prof. Ira Remsen, of Johns Hopkins University, who had planned the laboratory was then introduced. He made a very graceful address and at the close he thanked Mr. Kent in behalf of the chemists of the country for the substantial aid he had given the science in building so magnificent and complete a workshop.

Prof. J. U. Nef, under whose immediate supervision the laboratory had been built, and who planned most of the detail of the interior fittings was then introduced. He delivered an interesting address entitled, "Important Factors in the Development of a Research Laboratory."

At the conclusion of Prof. Nef's address, president Harper called on Prof. A. B. Prescott, of the University of Michigan, as the oldest teacher of chemistry present to make some remarks. Prof. Prescott delivered a brief impromptu address in his usual happy and pointed style. At the conclusion of the addresses a reception was held in the Halls of the laboratory.

The laboratory and equipment has cost Mr. Kent \$235,000.00, and it is very handsome, convenient and complete. It is to be hoped that the plan with detailed description will be published before long.

Mr. Kent is the brother of the founder of the Kent Chemical Laboratory, of Yale University. In the vestibule of the main entrance on the east wall in a handsome medallion bas-relief of Mr. Kent and below it is the dedicatory inscription which reads thus:

"This building is dedicated to a fundamental science in the hope that it will be a foundation stone laid broad and deep for the temple of knowledge in which as we live, we have life.—Sidney A. Kent."

On the morning of January 2, at nine o'clock, the visiting chemists assembled to hear the report of the committee appointed the night before at the dinner. The report provided for a conference of chemists to be held annually at such time and place as may be decided each year by the conference. No organization was made other than the formation of a standing

committee of three (3) members who are to make the necessary arrangements for the meeting, the chairman of the committee is to act as secretary of the conference. The committee for 1894 consists of Profs. J. U. Nef, P. S. Baker, and P. C. Freer. The object of the conference is to discuss methods of teaching and no papers on research are to be read. The meetings are to be arranged so as not to conflict with the meetings of the American Chemical Society and it was the sense of the meeting that whenever possible the conference should be held in conjunction with the meeting of the American Chemical Society.

The Winter Convocation of the University was held in Central Music Hall, January 2, at eight o'clock p. m. The convocation address being delivered by Prof. Ira Remsen who took as his subject, "The Chemical Laboratory." He spoke of the origin and development of the modern chemical laboratory and of the character of the work which had been done in the great laboratories of the world; of the work which had been accomplished in this country and of the prospects for the future. His address was highly entertaining and was enjoyed by a large audience composed of the faculties, official guests, students, and friends of the University. After the exercises a reception was held by the president in honor of Prof. Remsen in the foyer of the Music Hall.

The committee of arrangements who had charge of all of the exercises consisted of Profs. J. U. Nef, R. D. Salisbury, C. A. Strong, W. S. Stratton, and J. Loeb.

They are to be congratulated on the success of their management.

W. L. DUDLEY.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

AN ATTEMPT TO FIND THE AMOUNT OF PHOSPHORUS IN THREE SAMPLES OF STEEL.¹

BY CHAS. B. DUDLEY, AND F. N. PRASE, Chemist and Assistant Chemist,
Pennsylvania Railroad, Altoona, Pa.

SOMETHING over a year and a half ago, in connection with the preparation of a method for determining phosphorus in steel, to be used as a part of the specifications on which steel is bought, for the use of the Pennsylvania Railroad Company, we deemed it essential to know pretty accurately, the amount of phosphorus in each of three different samples of steel. The use made of the results finally obtained from these steels, is given in our paper, "On Some Points in the Determination of Phosphorus in Steel by the Volumetric Method," and what follows here, is an account of the various efforts made to get the desired information. It will be observed before we have finished, that what at first seemed a very simple thing, proved in the end to be a very difficult affair, and that after all the work done on the subject, the final result is still not entirely free from doubt.

The three samples of steel were as follows : No. 1 was boiler plate made by the open hearth process, and containing presumably about 0.15 per cent. of carbon, and less than 0.05 per cent. of phosphorus. No. 2 was a piece of a locomotive driving tire, made by the open hearth process, and containing presumably from 0.50 per cent. to 0.60 per cent. of carbon and

¹ Read at the Baltimore meeting, December 28, 1893.

from 0.05 per cent. to 0.07 per cent. of phosphorus. No. 3 was a crucible steel billet, containing presumably from 1.00 per cent. to 1.20 per cent. of carbon and less than 0.04 per cent. of phosphorus. Quite a quantity of drillings from each of these samples was prepared, care being taken to eliminate the influence of segregation as much as possible by (1) putting the drill holes entirely through the sample, and at right angles to the line of final solidification of the metal, (2) by having the drillings as fine as they could conveniently be made, and (3) by thoroughly mixing them.

The drillings having been obtained, our first thought was that we would find out the amount of phosphorus in these steels, by analyzing them ourselves, and by asking some other chemists of recognized ability, to do the same. Accordingly a quantity of the drillings was sent to four different chemists: Mr. A. A. Blair, 406 Locust street, Phila., Dr. T. M. Drown, Mass. Inst. Tech., Boston, Prof. J. W. Langley, Case school of Applied Science, Cleveland, O., and Mr. A. S. McCreath, Harrisburg, Pa. Blair used the acetate method; Drown the molybdate-magnesia method; McCreath the acetate method; Langley both these methods, and we ourselves used the molybdate-magnesia method on all the samples, and the acetate method on the No. 2 sample. We are without information as to the exact details of the methods used by the other chemists. In our own case we used the molybdate-magnesia method, exactly as described in Fresenius' Quantitative Analysis, second American edition, John Wiley and Sons, p. 763, except that we used five grams dissolved in concentrated nitric acid, instead of aqua regia, and heated to 200° C. in an air bath, as suggested by Blair in The Chemical Analysis of Iron, second edition, p. 90, in order to destroy carbonaceous matter. In using the acetate method we proceeded exactly as described in The Chemical Analysis of Iron, by A. A. Blair, second edition, p. 81, and following. We give below the results that have been obtained on these three samples of steel, in accordance with the above, as follows:

| | No. 1.
Per cent. | Steel.
No. 2.
Per cent. | No. 3.
Per cent. |
|--|---------------------|-------------------------------|---------------------|
| Blair..... | 0.035 | 0.048 | 0.029 |
| Another operator..... | 0.035 | 0.047 | 0.027 |
| Third operator | 0.035 | 0.047 | 0.028 |
| Drown, average of duplicates..... | 0.037 | 0.050 | 0.030 |
| McCreath | 1.... 0.035 | 0.045 | 0.027 |
| | 2.... 0.035 | 0.046 | 0.028 |
| Langley.. { Acetate method | 1.... 0.042 | 0.053 | 0.019 |
| " " | 2.... | | 0.020 |
| { Another operator... | 1.... 0.042 | 0.050 | 0.019 |
| " " | 2.... 0.042 | 0.056 | 0.020 |
| Langley, molybdate magnesia | 0.040 | 0.053 | 0.022 |
| Dudley { Molybdate magnesia | 1.... 0.041 | 0.056 | 0.033 |
| and 2.... 0.042 | | 0.056 | 0.032 |
| Pease 3.... 0.041 | | 0.056 | 0.033 |
| { Acetate method | 1.... | 0.047 | |
| | 2.... | 0.046 | |
| | 3.... | 0.046 | |

It will be observed that these results are hardly as satisfactory as could be desired, and that if we must know as we very greatly desired to do, within a couple of thousandths of a per cent. the amount of phosphorus actually in these steels, we were thus far without this information. The extreme variation on the No. 1 steel, is from 0.035 per cent. to 0.042 per cent. a difference of 0.007 per cent. the average of the thirteen determinations being 0.0386 per cent. On the No. 2 steel, the range is from 0.045 per cent. to 0.056 per cent. a difference of 0.011 per cent., the average of the sixteen determinations being 0.0512 per cent. On the No. 3 steel, the range is from 0.019 per cent. to 0.033 per cent., a difference of 0.014 per cent., the average of the fourteen determinations being 0.0262 per cent.

In view of these results some further study was put upon the matter. It will be observed that in our own hands, the molybdate-magnesia method, and the acetate method, do not give the same results, nor do they give the same results in the hands of Langley, and we accordingly were somewhat in doubt, as to which method gave the most reliable results. In order to locate if possible the difficulty, we examined all the residues obtained, in the course of the acetate method, and to our astonishment we found phosphorus in three different places, which we will now describe.

I. It will be remembered that after the phosphorus is separated from the bulk of the iron, by means of the basic acetate precipitate, there is quite a volume of filtrate, containing iron in the protoxide form. This filtrate was allowed to stand in the beaker for a couple of days covered, and at the end of this time, the bottom of the beaker contained quite a precipitate of apparently hydrated sesquioxide of iron, which separated on standing. This precipitate was filtered off, and dissolved in dilute nitric acid and tested with molybdate solution. In no case did we fail to get a little yellow precipitate, apparently indicating that the amount of sesquioxide of iron obtained in the solution, before the basic acetate separation is made, is not quite sufficient to, or does not succeed in carrying down all the phosphorus. The directions require that a few drops of bromine water should be added, to oxidize enough iron to combine with the phosphorus, which was carefully done in every case, but so far as these experiments go, they seem to indicate that some of the phosphorus is still left behind.

II. It will be remembered that the basic acetate precipitate, is dissolved on the filter in hydrochloric acid. In our working of the acetate method, we found in a number of cases, a slight amount of material left undissolved on the filter. On collecting the filters from a number of determinations, burning off the filters, dissolving with nitric acid, and testing with molybdate, a clear reaction for phosphorus was obtained. It should be stated that the stain left on the filter paper, after dissolving in hydrochloric acid, is not in our experience universal. Under certain conditions the basic acetate precipitate apparently goes up with greater difficulty, than with others. It is also claimed that when titanium is present in iron or steel the basic acetate precipitate usually leaves a stain on the filter.

III. The filtrate from the ammonium magnesium phosphate, which it will be remembered contains some iron, and some citric acid, was treated with dilute nitric acid and evaporated to dryness on the steam table. The residue was taken up with dilute nitric acid and treated with molybdate, and here a voluminous yellow precipitate was obtained.

These experiments seemed to indicate that, in our hands at

least, the acetate method did not give quite all the phosphorus, and helped to explain the discrepancy between the molybdate-magnesia method and the acetate method. The bulk of the yellow precipitate obtained in the three places above described, especially from the citric acid filtrate, was so considerable that it seemed almost possible to get a sufficient amount of phosphorus from it to weigh, and we accordingly made three more determinations on ten (10) grams each of the No. 2 steel, by the regular acetate method, obtaining as the average of the three 0.045 per cent. The residues from the three places above described from these thirty (30) grams of steel were all collected together and the phosphorus separated from these residues by means of molybdic acid. The yellow precipitate obtained was then treated with magnesia mixture in the regular way. The results gave a percentage of 0.0053 per cent. phosphorus, and this added to the amount obtained by the direct acetate method gave the phosphorus in the No. 2 sample 0.0503 per cent. This figure it will be observed is 0.006 per cent. less than the average which we obtained on the same sample by the regular molybdate-magnesia method.

It has generally been conceded, we think, that the molybdate-magnesia method for determining phosphorus, following Fresenius, is liable to give rather high results, especially if arsenic is present and is not separated, which we did not do. We did separate the possible traces of silica from the magnesium pyrophosphate as Fresenius recommends. We were therefore still in doubt as to the amount of phosphorus in these steels, and did not feel satisfied to use any of the results obtained.

The question therefore arose with renewed force, how shall we find out how much phosphorus these three steels contain? After considerable study and discussion, the following method was decided on; namely, start with ten grams, and proceed exactly as described in the Chemical Analysis of Iron and Steel, above mentioned, up to the point of adding the bromine. Then instead of adding a few drops, add enough bromine water to convert half a gram of the iron into the sesquioxide. Then make the basic acetate separation as described, except on account of the large amount of iron, a little ammonium acetate is

added. Dissolve the basic acetate precipitate in moderately strong hydrochloric acid, and evaporate the liquid to dryness, to render any silica present, insoluble. Take up with forty cc. of strong nitric acid, and evaporate to dryness a second time, to remove the hydrochloric. Then take up with seventy-five cc. of dilute nitric acid, 1.13 sp. gr., filter, and precipitate with seventy-five cc. of molybdate mixture, with the proper precautions of the molybdate-magnesia method as to temperature and time. Collect the yellow precipitate on a filter, and after thorough washing dissolve in $2\frac{1}{2}$ cc. of strong ammonia diluted with water, and wash thoroughly with water until the total volume of solution amounts to about 100 cc. Pass hydrogen sulphide until this solution becomes dark red in color. The hydrogen sulphide readily converts the molybdic acid into molybdenum sulphide, in ammoniacal solution, and if the gas has been passed long enough, a complete separation of the molybdic acid results when the solution is treated with hydrochloric acid in slight excess. Filter off from the molybdenum sulphide, wash thoroughly with water containing a little hydrochloric acid, and evaporate nearly to dryness, in order to have controllable bulk of solution. Then take up with a little water, to which two or three cc. of dilute hydrochloric acid has been added, and filter if necessary to remove separated sulphur and a trace of molybdenum sulphide which may separate during the evaporation. Concentrate the filtrate to about fifteen cc., and add five cc. of magnesia mixture, and a little ammonia. The total volume of the solution should not now exceed twenty-five or thirty cc. The ammonium magnesium phosphate from this point is treated in the regular way.

The three samples of steel above referred to treated in this way, gave the following figures:

| | No. 1.
Per cent. | No. 2.
Per cent. | No. 3.
Per cent. |
|------------------|---------------------|---------------------|---------------------|
| Phosphorus | 1..... 0.040 | 0.053 | 0.032 |
| | 2..... 0.040 | 0.054 | 0.033 |

Unfortunately the separated oxide of iron from the filtrates in the basic acetate separation, in the cases of these determinations were not examined, but subsequent examinations of this material on other samples has shown that half a gram of iron

carries down all the phosphorus, or possibly all but the merest trace. Also in the case above mentioned, nothing was left on the filter when dissolving the basic acetate in hydrochloric acid. An examination of the filtrate from the magnesium phosphate precipitate in no case failed to show a slight yellow precipitate, and these results have been confirmed by quite a number of subsequent examinations. The amount of this, however, is very slight, the bulk of the yellow precipitate obtained being very much less than is shown in the citric acid filtrate when the acetate method is used. It seems probable therefore, that notwithstanding all the precautions involved in the method described above, the results given are still a trifle low. These figures were, however, taken as representing the phosphorus content of these three samples of steel.

The method finally used on these steels, and whose results we regard as the most reliable, will be at once recognized as a modification of the combination method, first proposed by Riley, and subsequently described in detail by J. Lawrence Smith in the *American Journal of Science*, **123**, 316. This combination method seems to have several advantages and perhaps to unite, in a sense at least, the best features of the acetate and the molybdate-magnesia methods. The acetate method is used to concentrate the phosphorus from a large amount of material, into a very small amount of iron. The molybdate method is used to separate the phosphorus from the iron. The conversion of the molybdic acid into sulphide in ammoniacal solution is due to a suggestion of Hundeshagen. It will be observed that by the method as we actually used it there are two opportunities to get rid of arsenic; *viz.*, before the basic acetate precipitation is made, and also along with the molybdenum sulphide. Subsequent experiments seemed to indicate that the first of these two separations can be omitted with safety. The method is long and laborious, but seems to offer, all things considered, perhaps the most accurate means now known of determining small amounts of phosphorus in steel. It may be well to add that on coming subsequently to determine phosphorus in these three steels by the volumetric method, a difficulty was found with the No. 2 steel. This will appear by a comparison of the

results obtained on the three steels by the two methods, as follows:

| | No. 1.
Per cent. | No. 2.
Per cent. | No. 3.
Per cent. |
|-------------------------|---------------------|---------------------|---------------------|
| Combination method.... | 0.040 | 0.053 | 0.032 |
| Volumetric method | 0.040 | 0.059 | 0.032 |

In view of this discrepancy an arsenic determination was made on the No. 2 steel, following exactly the method described in *The Chemical Analysis of Iron*, p. 188, except that we started with fifty grams. The result obtained was

| | No. 2.
Per cent. |
|---------------|---------------------|
| Arsenic | 0.009 |

This result seems to indicate that arsenic is the cause of the discrepancy in the No. 2 steel, and apparently confirms again the view that arsenic interferes with the determination of phosphorus by means of molybdic acid.

It is perhaps not essential but may not be amiss to say that where the amount of phosphorus is large a difficulty may arise with the combination method, if ten grams are used to start with, due to the large bulk of molybdenum sulphide obtained. Very large amounts of molybdenum sulphide are difficult to wash clean. Of course the difficulty is easily overcome by starting with less than ten grams.

ON SOME POINTS IN THE DETERMINATION OF PHOSPHORUS IN STEEL BY THE VOLUMETRIC METHOD.¹

BY CHAS. B. DUDLEY AND F. N. PEASE, Chemist and Assistant Chemist,
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ONE of the most common methods of separating phosphorus from iron, either in ores, pig iron, wrought iron or steel, is by means of molybdic acid, the separation giving rise to the well-known yellow precipitate of ammonium phosphomolybdate. The subsequent treatment of this yellow precipitate is very varied. Some chemists prefer to dissolve the precipitate in ammonia, and then determine the phosphoric acid by means of magnesia mixture. Others prefer to weigh the yellow precipitate just as obtained, and some even to measure the volume of

¹ Read at the Baltimore meeting, December 28, 1893.

this yellow precipitate in a specially graduated apparatus. Perhaps however, by far the largest number of chemists, prefer to treat the yellow precipitate by some volumetric method, either what may be called the alkali method, described by Handy in the *Proceedings of the Engineer's Society of Western Penna.*, 8, 78, or the perhaps better known permanganate method, described by Emmerton, published in the *Trans. A. I. M. E.*, 15, 93, and subsequently modified by Wood, Shimer, Drown, Jones, and others. We use the permanganate method. This method as we prefer to use it, and with all the precautions which we deem essential to secure uniform and accurate results, except as to the interference produced by arsenic, has been published in the *J. Anal. Appl. Chem.*, 7, 108, and also in the *J. Am. Chem. Soc.*, 15, 519. What follows is a discussion of some points suggested by the work done preliminary to drawing up the method above referred to.

In order that what is given may be clearly understood, it may not be amiss to state that by this method, the steel is dissolved in nitric acid of 1.13 sp. gr., the solution boiled a few seconds, and then treated with potassium permanganate to destroy carbonaceous matter, and possibly secure complete oxidation of the phosphorus; the separated manganese oxide, reduced by a few crumbs of ferrous sulphate, the solution then heated to a definite temperature, and a measured volume of molybdate solution, which is likewise at a definite temperature, added, the vessel enclosed to prevent loss of heat, and shaken vigorously for five minutes, allowed to stand a few minutes for the precipitate to settle, and then filtered. After thorough washing with acid ammonium sulphate wash water, the yellow precipitate is dissolved in ammonia, the solution treated with a definite amount of sulphuric acid, and then passed through the reductor, and finally titrated with potassium permanganate of known strength, the amount of phosphorus being ultimately obtained by multiplying the number of cubic centimeters of permanganate used by the proper factor.

It is obvious that the accuracy of the determination by the method briefly outlined above, depends on several conditions:

I. Is all the phosphorus in the steel taken to start with

actually in the yellow precipitate obtained, or in other words, can phosphorus be completely separated from iron by molybdic acid? Upon this point we have done no work, and cannot express an opinion. The late J. Lawrence Smith used to claim that the complete separation of very small amounts of phosphorus from large amounts of iron by means of molybdic acid was at least doubtful, and that the most reliable procedure consisted in first concentrating the phosphorus into a very small amount of iron, and then separating it from this iron by means of molybdic acid. Assuming, however, that all the phosphorus in the steel is in the yellow precipitate, several further questions arise.

II. Is the yellow precipitate of constant composition, that is, is it independent of the conditions under which it is formed? It is obvious that this is a very important point for all those methods which either weigh or measure the yellow precipitate, and also for the permanganate volumetric method, which in reality actually measures not the phosphorus or phosphoric acid in the yellow precipitate but rather the molybdic acid, the phosphorus being determined from its relation to the molybdic acid. If now the yellow precipitate is not of constant composition, or more definitely if the relation between the phosphorus and molybdic acid in this precipitate is not a constant one, but is affected by the conditions under which the precipitate is formed, it is clear that these conditions must be definitely defined, and always closely followed, or there will be great uncertainty in the results. What then are the facts in the case? It is well known that almost from the beginning of the use of molybdic acid in phosphorus determinations there has been more or less uncertainty as to the constitution of the yellow precipitate, and especially that, depending on the conditions, it is very liable to be contaminated with free molybdic acid. Furthermore, Emmerton has apparently demonstrated in the place cited above, that the temperature of precipitation has a very important influence on the final result. He also claims that the amount of free acid in the solution, the concentration of the solution, and the length of time allowed for precipitation also affect the final result. Other workers, especially Wood, in the

J. Anal. Chem., 1, 138, Shimer, *Trans. A. I. M. E.*, 17, 100, and Drown, *Trans. A. I. M. E.*, 18, 90, have put a good deal of study on the method. None of the determinations given that we have been able to study, show that the final result is independent of the conditions under which the yellow precipitate is obtained. We ourselves have made a good many experiments, varying the conditions under which the yellow precipitate is obtained, and feel safe in saying that almost any variation in the conditions will produce some difference in the final result. Much of our work simply confirms that of other operators. Perhaps it would be worth while to give a single illustration.

Two sets of one gram each, of three samples of steel containing different amounts of carbon and phosphorus were dissolved in seventy-five cc. of 1.13 sp. gr. nitric acid, and further treated exactly alike according to our standard method above referred to, except that before adding the molybdate solution, ten cc. of strong ammonia was added to each flask of one set. This procedure would as is evident, result in the formation of the yellow precipitate in one set in a menstruum containing more ammonium nitrate, and less free nitric acid than the other contained. The results obtained are as follows, the figures being the phosphorus in the three steels:

| | No. 1
steel.
Per cent. | No. 2
steel.
Per cent. | No. 3
steel.
Per cent. |
|-------------------|------------------------------|------------------------------|------------------------------|
| Without ammonia.. | 1..... 0.036 | 0.055 | 0.029 |
| | 2..... 0.037 | 0.055 | 0.029 |
| | 3..... 0.037 | 0.055 | 0.030 |
| With ammonia..... | 1..... 0.047 | 0.064 | 0.036 |
| | 2..... 0.043 | 0.062 | 0.033 |
| | 3..... 0.045 | 0.067 | 0.039 |

The difference in the results is quite marked. Diminution in free acid and increase in ammonium nitrate apparently leads to higher figures and less uniformity in duplicate determinations. Some of our experiments indicate that even a much less change in the proportions of free acid and ammonium nitrate than given above affects the final result. Also that in addition to the variables mentioned above, a different result is obtained when sugar or other organic substance is used to reduce the separated manganese oxide than is given when ferrous sulphate

is used. Finally there are quite strong indications, that the total amount of molybdic acid present in the solution and even its state of oxidation have an influence on the final figures obtained.

If it be allowed then that the conditions, under which the yellow precipitate is formed affect its constitution, or more definitely, affect the ratio between the molybdenum and phosphorus in this precipitate, or what amounts to the same thing, affect the final result, two things are evident.

1. In order to secure accurate and concordant results, it is necessary that the conditions under which the yellow precipitate is obtained shall be very clearly and sharply defined, and that on making the analyses, these conditions shall be very rigidly maintained.

2. It will not do to use ratios based on the analysis of the yellow precipitate obtained under one set of conditions as a means of calculation for precipitates obtained under another and different set of conditions.

As an example of this second statement, it seems clear, if the preceding views are correct, that if a chemist obtains a quantity of the yellow precipitate from sodium phosphate with no iron present, and the conditions entirely different from those which prevail in the determination of phosphorus in steel, and then makes an analysis of this yellow precipitate to determine the ratio between molybdic acid and phosphorus, although the figures he obtains may be quite accurate, he is still not at liberty to use these figures in determining phosphorus in iron and steel and claim that they give accurate results. It is of course conceded that they may be accurate but there is no certainty of this. It should be stated that the amount of phosphorus in the yellow precipitate is so small, and the amount of molybdic acid is so large, that there is room for considerable variation in ratios without giving rise to very serious differences in results, especially in steels low in phosphorus. This fact may help to account for the claim so generally made by different chemists that their results agree within reasonable limits of error with those of other good chemists. But if it is desired to obtain fairly accurate and concordant results, we see no way of escaping from the two statements given above.

If these points be conceded it is obvious that a still further very important question arises; *viz.*,

III. How shall the proper factor for use with the permanganate of potash be obtained? It is clear, since the permanganate of potash solution is standardized against metallic iron, that we need two ratios, first, the ratio between molybdic acid and iron, and second, the ratio between molybdic acid and phosphorus in the yellow precipitate obtained under definite conditions. What then are these ratios? On looking over the literature on the subject, we find two or three serious uncertainties. The ratio between iron and molybdic acid is evidently affected by the change which takes place in the molybdic acid when it passes through the reductor, and we do not find that there is agreement between those who have worked on this point. Furthermore, Jones has apparently shown in the *Trans. A. I. M. E.*, 18, 705, that the use of the reductor gives different results than are obtained when the molybdic acid in the yellow precipitate is reduced by granulated zinc in a beaker as originally proposed by Emmerton. Again the published ratios between molybdic acid and phosphorus, vary between 100: 1.54 and 100: 1.90 if we may use our own figures for illustration. It is clear therefore that there are two difficulties in the way of using any of the published ratios, first, which ratios shall be used, and second, the point already discussed quite at length, that these ratios vary, or at least the final results vary according to the conditions under which the yellow precipitate is obtained.

Two methods of procedure are clearly open to us.

First, obtain a quantity of the yellow precipitate under the conditions which we deem essential, and then make independent determinations of the phosphorus and molybdic acid in this precipitate. This would give the ratio between these two constituents. Then pass a quantity of the same precipitate through the reductor and titrate with permanganate. This will give the ratio between molybdic acid and iron. This we have not done yet, partly for lack of time and partly from the difficulties of the analysis. In our experience it is not easy to dry and weigh the yellow precipitate without its undergoing change in the process, and our experience with methods of determining

molybdic acid is also meager. There is need of some good and careful work on this point.

In view of these uncertainties, we choose the other method of procedure; *viz.*,

Second, determine the phosphorus in several samples of steel by the most accurate known gravimetric method, then make an analysis for phosphorus in these same steels by the volumetric method, and then use such a factor with the potassium permanganate as will bring these results together. The work done on the steels chosen for this purpose is given in our paper "On an Attempt to Find the Amount of Phosphorus in Three Samples of Steel."

It is evident that this procedure, while it enables us to get a factor to use with the potassium permanganate in the phosphorus determinations by the volumetric method as we use it, does not throw any light on the ratios between iron and molybdic acid, and between molybdic acid and phosphorus in the yellow precipitate as we obtain it. But if we assume that the ratio of iron to molybdic acid is 100:90.76 it follows that the ratio of molybdic acid to phosphorus in the yellow precipitate as we obtain it is 100:1.90 and this is the calculation which we have used in our published volumetric method above referred to.

One further question may arise; *viz.*, in view of the apparent variability of the yellow precipitate according to the conditions under which it is obtained.

IV. If the conditions are made constant, will the results obtained be uniform and agree with each other?

In reply to this we may say that so far as our experience has gone, the agreement between duplicate determinations on the same sample of steel where the conditions of the method as published are rigidly adhered to, rarely exceeds more than a couple of thousandths of a per cent., also different operators using the published method on the same sample of steel, after a little experience is obtained with it, rarely disagree more than three or four thousandths.

THE EXACT DETERMINATION OF PHOSPHORUS BY THE MOLYBDATE METHOD IN IRON, STEEL, AND ORES, WHICH CONTAIN ARSENIC.¹

By JAMES O. HANDY, Chemist of The Pittsburgh Testing Laboratory, L't'd.

CLASSIFICATION OF EXISTING METHODS FOR PHOSPHORUS.

1. The acetate method of Blair and others.
2. The molybdate methods.
 - (a) Methods in which the phosphomolybdate is weighed (methods of E. F. Wood and others).
 - (b) Methods in which the amount of yellow precipitate is estimated volumetrically.
 - (a') By permanganate (methods of Emmerton, Drown, Jones, and others).
 - (b') By alkali (methods of Manby, Handy, and others).
3. The combination methods.
 - (a) The acetate and molybdate methods.
 - (b) The molybdate and magnesia methods.

In the "acetate" methods the phosphorus is precipitated as phosphate, after separating by hydrogen sulphide, any arsenic which is present. The methods are long and the manipulation difficult.

In the "molybdate" methods, the phosphorus is precipitated as ammonium phosphomolybdate and weighed or titrated. Arsenic, which is believed to be of rare occurrence, is disregarded. It is, however, a fact, that, when arsenic is present in a solution from which phosphorus is precipitated as phosphomolybdate, a portion of the arsenic accompanies and contaminates the phosphorus precipitate.

The "molybdate" methods are in general, very short and their manipulation simple; they are widely used. With the drawback of arsenic interference removed, the molybdate method takes front rank for simplicity, brevity and accuracy.

¹ Read at the Baltimore meeting, December 28, 1893.

TABLE I.
EXTENT OF THE INTERFERENCE OF ARSENIC IN PHOSPHORUS
DETERMINATIONS.

| Substance analyzed. | Phosphorus per cent. contained. | Arsenic per cent. contained. | Method. | Temperature of precipitation. | Apparent per cent. phosphorus. | Error caused by arsenic. | Remarks. |
|---------------------|---------------------------------|------------------------------|---|-------------------------------|--------------------------------|--------------------------|-----------------------|
| Steel | 0.096 | 0.050 | J. O. Handy | 85° C. | 0.094 | None | Within limit of error |
| " | 0.096 | 0.050 | " | " | 0.095 | " | " |
| " | 0.098 | 0.100 | " | " | 0.098 | " | " |
| " | 0.098 | 0.100 | " | " | 0.099 | " to 0.001 | " |
| " | 0.096 | 0.250 | " | " | 0.099 | 0.003 | " |
| " | 0.096 | 0.350 | " | " | 0.102 | 0.006 | " |
| " | 0.096 | 0.500 | " | " | 0.106 | 0.010 | " |
| " | 0.096 | 0.750 | " | " | 0.111 | 0.015 | " |
| " | 0.096 | 1.870 | " | " | 0.125 | 0.029 | " |
| " | 0.012 | 0.100 | " | " | 0.012 | " | " |
| " | 0.012 | 0.500 | " | " | 0.011 | " | " |
| " | 0.012 | 1.000 | " | " | 0.011 | " | " |
| Pig iron | 0.036 | 0.100 | " | " | 0.039 | 0.003 | " |
| " | 0.036 | 0.150 | " | " | 0.043 | 0.007 | " |
| " | 0.083 | 0.100 | " | " | 0.088 | 0.005 | " |
| " | 0.083 | 0.150 | " | " | 0.094 | 0.011 | " |
| " | 0.297 | 0.500 | { and we'h'g } | " | 0.315 | 0.018 | " |
| Ferro-mang'se | 0.292 | 0.500 | { evaporat'n
neutraliz'n
weighing } | " | 0.313 | 0.021 | " |
| Iron ore | 0.096 | 0.500 | " | " | 0.135 | 0.038 | " |
| Mang'se ore | 0.212 | 0.500 | " | " | 0.264 | 0.052 | " |

EXPERIMENTS PROVING THAT ARSENIC DOES NOT PRECIPITATE WHEN LITTLE OR NO PHOSPHORUS IS PRESENT.

Experiments.—Two grams of magnetic iron ore, (a very pure concentrate), showed 0.002 per cent. phosphorus. A duplicate containing 0.500 per cent. of arsenic, in the fully oxidized form, showed also exactly 0.002 per cent. of phosphorus.

The filtrate, which contained arsenic, was heated for a short time to 60°–70°C. before molybdic acid or arsenomolybdate began to separate. The same result was repeatedly obtained with arsenical filtrates from phosphomolybdate precipitates.

A solution of arsenic acid in nitric acid, properly prepared as for phosphorus determination gives no precipitate at 85° C. with molybdate solution unless the heating is continued.

The experiments described prove very clearly that the precipitation of arsenic with phosphomolybdate is a mechanical one; that the arsenic is only *dragged* down. With little or no phosphorus, no arsenic precipitates.

The case is parallel to the contamination of the first ferric

hydroxide precipitate, with lime, or of the first oxalate of lime precipitate, with magnesia.

In these cases, solution and re-precipitation of the contaminated precipitates, effects their purification.

Experiments (Table II) prove that the same treatment properly applied, is equally efficient in purifying arsenical phosphomolybdate.

The exact method of procedure follows:

TABLE II.
ELIMINATION OF ARSENIC FROM PHOSPHOMOLYBDATE.

| Substance analyzed. | Phosphorus contained. | Arsenic contained. | Method. | Temperature of precipitation. | | Phosphorus found. | Error. |
|---------------------|-----------------------|--------------------|--------------------------------|-------------------------------|--------|-------------------|--------|
| | | | | First | Second | | |
| Steel | 0.096 | 0.500 | J. O. Handy | 80° C. | 75° C. | 0.096 | none |
| " | 0.096 | 0.500 | " | " | " | 0.096 | " |
| " | 0.096 | 0.500 | " | " | " | 0.097 | 0.001 |
| " | 0.096 | 1.000 | " | " | " | 0.097 | 0.001 |
| " | 0.096 | none | " | " | " | 0.095 | 0.001 |
| " | 0.096 | " | " | " | " | 0.095 | 0.001 |
| " | 0.096 | " | " | " | " | 0.094 | 0.002 |
| " | 0.096 | 0.500 | " | 85° C. | 85° C. | 0.097 | 0.001 |
| " | 0.096 | 0.500 | " | " | 80° C. | 0.094 | 0.002 |
| " | 0.038 | 0.500 | " | 80° C. | 75° C. | 0.036 | 0.002 |
| " | 0.038 | 0.500 | " | " | " | 0.037 | 0.001 |
| " | 0.038 | 0.500 | " | " | " | 0.039 | 0.001 |
| " | 0.038 | none | " | " | " | 0.037 | 0.001 |
| Pig iron | 0.082 | 0.500 | " | " | " | 0.081 | 0.001 |
| " | 0.082 | 0.500 | " | " | " | 0.081 | 0.001 |
| Ferro-mang'se | 0.282 | 0.500 | { evaporat'g }
{ weighing } | 85° C. | 75° C. | 0.281 | 0.001 |
| Pig iron | 0.286* | 0.500 | J. O. H. and " | " | " | 0.289 | 0.003* |
| Iron ore | 0.083 | 0.500 | Evap. " " | " | " | 0.085 | 0.002 |
| Manganese | 0.199 | 0.500 | " " " | " | " | 0.200 | 0.001 |

* NOTE.—A little lost.

THE METHOD OF REDISSOLVING THE PHOSPHOMOLYBDATE AND FREEING IT FROM ARSENIC.

Having separated the phosphorus as phosphomolybdate by any good method and washed it well with one per cent. nitric acid, place a twelve ounce Erlenmeyer flask under the funnel.

Dissolve the yellow precipitate by ammonium hydroxide wash (1:6), using about fifteen cc. in all, and wash it into the flask. Dilute the solution to about seventy-five cc. and heat to 75° C. and add a mixture of ten cc. HNO₃ (1.42) and twenty-five cc. of molybdate solution (E. F. Wood's formula), shake well, filter and wash

- (a) with one per cent. nitric acid, dry and weigh, or
- (b) with one per cent. nitric acid and $\frac{1}{10}$ per cent. potassium nitrate, dissolve and titrate (Handy's method).

The greater part of the analytical work of this paper has been done by my assistant, Mr. Geo. O. Loeffler.

METHODS USED.

For Steel and Pig-iron.—The method used in all analyses of steel and pig-iron, was the one published by the author in 1892 (*Trans. Engineer's Society of Western Pennsylvania* March, 1892, and *J. Anal. Appl. Chem.*, April, 1892).

For Ferromanganese.—Two grams, dissolved in nitric acid, (1.42), and the solution evaporated to dryness. The residue, having been redissolved in hydrochloric acid, (1.20) the solution was diluted and filtered. The filtrate was treated with ammonium hydroxide till ammoniacal, then acidified with nitric acid, heated to 85° C. and precipitated with fifty cc. of molybdate solution.

For Iron and Manganese Ores.—Two grams dissolved in aqua regia (five per cent. HNO_3 , (1.42) and ninety-five per cent. HCl (1.20), and the solution evaporated to dryness. Subsequent procedure was as described above for ferromanganese after the evaporation. Phosphorus, in "insoluble residues" was separated and determined.

Arsenic was added as dry As_2O_3 to the samples when weighed out. The reagents used in the analysis oxidized it to arsenic oxide.

NOTES AND QUERIES ON DR. DUDLEY'S METHOD OF DETERMINING PHOSPHORUS IN STEEL.

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THE object of the work outlined in this paper was to ascertain the accuracy of the method proposed by Dr. Dudley for the volumetric analysis of phosphorus in steel, described in *J. Am. Chem. Soc.*, Sept., 1893, p. 519, and to determine if a separation of phosphorus could be made in the presence of arsenic with a sufficient degree of accuracy for commercial purposes

by this method or any modification of it.

Our first undertaking was to ascertain if the new ratio between phosphorus and molybdic acid in the yellow precipitate of 1.90, brought forward by Dr. Dudley, was correct. The commonly accepted factor as found by Emmerton and others is 1.794, *Trans. A. I. M. E.*, 15, 93, R. Finkener, *Ber. d. Chem. Ges.*, 11, 1638, Henry Pemberton, *Chem News*, 46, 4, Von der Pfordten, *Ztsch. anal. Chem.*, 23, 422, and very recent work by H. C. Babbitt, *J. Anal. Appl. Chem.*, 7, 165, has confirmed this ratio. However, as Dr. Dudley used an entirely different method for determining this ratio, we have followed as nearly as possible his work as outlined in the *American Engineer and Railroad Journal*, Jan. 1893, p. 18, but have been wholly unable to obtain his figure.

Determination of the Ratio between Phosphorus and Molybdic Acid in the Yellow Precipitate.—Four samples of steel of very different carbon composition were taken, and the phosphorus determined both gravimetrically and volumetrically in each, and from the figures obtained, the ratio between the phosphorus and the molybdic acid in the yellow precipitate, formed in the volumetric analysis under the conditions used, was computed. The complete analyses of the steel used in this and subsequent investigations are as follows:

| | Carbon,
per cent. | Manganese,
per cent. | Silicon,
per cent. | Gravimetric
phosphorus,
per cent. | Sulphur,
per cent. |
|-------------|----------------------|-------------------------|-----------------------|---|-----------------------|
| No. 27.... | 0.188 | 0.321 | 0.020 | 0.110 | 0.052 |
| No. 789.... | 0.997 | 0.427 | 0.226 | 0.021 | 0.024 |
| No. 344.... | 0.588 | 1.295 | 0.079 | 0.065 | 0.107 |
| No. 65.... | 0.166 | 0.577 | 0.072 | 0.012 | 0.025 |

For our gravimetric determination we used the combination method as described by Dr. Dudley. The acetate method was followed up to the point of obtaining the basic acetate precipitate, at which stage enough bromine water was added to oxidize fully one-half a gram of iron, and the solution boiled. It was then cooled down and the acetate precipitation made exactly as described in Chemical Analysis of Iron, by A. A. Blair. This precipitate was dissolved in hydrochloric acid, and all traces of iron washed from the paper. After expelling the hydrochloric acid from the filtrate by repeated evaporations with nitric acid, seventy-five cc. of nitric acid 1.135 sp. gr. were added, the solu-

tion boiled, oxidized with potassium permanganate, and reduced with ferrous sulphate, as described in Dr. Dudley's routine method. The solution at 85° C. was then treated with seventy-five cc. of molybdic acid at 27° C., the yellow precipitate shaken down, filtered, and washed free of molybdic acid. We test for the presence of molybdic acid as follows: About four cc. of the acid wash water are caught in a test tube as they run through the filter, and treated with a few drops of dilute ammonium sulphide. The least presence of molybdic acid will cause the liquid to darken slightly. The cloud of sulphur produced by the addition of ammonium sulphide to the acid solution does not interfere in any way with the delicacy of the test. We have found this test far more sensitive than the one used by Dr. Dudley, who allows the acid wash water to drop into a dilute solution of ammonium sulphide, the test thus being in the alkaline solution. We have frequently found yellow precipitates which according to the alkaline solution test were thoroughly washed, yet with the acid test show unmistakable signs of molybdic acid which required one or two more washings to remove. The yellow precipitate was then dissolved in ammonia and saturated while warm with hydrogen sulphide, and the red solution of molybdenum sulphide slightly acidified with hydrochloric acid. The precipitate of molybdenum sulphide was allowed to settle, then filtered off rapidly on a large folded filter, avoiding contact with the air as much as possible, and washed thoroughly with strong hydrogen sulphide water containing a little hydrochloric acid. The large filtrate was then evaporated, and on boiling, it was invariably found that a small amount of molybdenum sulphide separated out. This was filtered off and the resulting filtrate concentrated to a bulk of about four cc. The phosphorus was then precipitated with from five to eight cc. of magnesia mixture and a small amount of ammonium hydroxide, the cold solution being vigorously stirred until precipitation began, when ammonium hydroxide amounting to one-third of the bulk of the solution was added, and the analysis allowed to stand for twelve hours. The precipitate was then filtered off, washed with ammonium nitrate until free from chlorine, and ignited. This precipitate was invariably contaminated with molybdic acid. It

was purified by dissolving in hot dilute hydrochloric acid, filtering, evaporating the filtrate to a small bulk, and precipitating as before. For our volumetric determination of the phosphorus in these samples we followed the preceding method up to the point of obtaining the ammoniacal solution of the yellow precipitate. This solution was acidified with sulphuric acid, passed through the reductor and titrated with permanganate, one cc. of which equals 0.003350 grams iron, and assuming as Dr. Dudley has, that the ratio between iron and molybdic acid is 90.76, the commonly accepted factor, we obtain the results in the table below.

| No. | Permanganate
used by volumet-
ric method,
cubic centimeters. | Phosphorus
by gravimetric
method,
per cent. | Ratio between
phosphorus
and molybdic
acid. | Error in ratio for
each 0.001 per cent.
error in gravimetric
determination. |
|-----------|---|--|--|--|
| 27..... | 103.1 | 0.110 | 1 : 1.759 | 0.016 |
| " 789.... | 19.0 | 0.021 | 1 : 1.826 | 0.087 |
| " 344.... | 59.4 | 0.065 | 1 : 1.813 | 0.027 |
| " 65.... | 11.2 | 0.012 | 1 : 1.806 | 0.151 |

A glance at the ratios obtained between phosphorus and molybdic acid in the above table will show that they are very irregular, but this will be explained by the last column of figures which point out that the gravimetric determinations of phosphorus must be made with absolute accuracy in order to have these ratios agree. The only point we wish to call attention to in the above table of ratios is the fact that they are all much lower than the ratio 1.90 proposed by Dr. Dudley, and obtained by him in a similar manner.

Not satisfied with the above results, we turned our attention to the actual analysis of the yellow precipitate, which was prepared for our investigations as follows: To a solution of ferric nitrate in nitric acid of 1.135 sp. gr., was added a sufficient amount of phosphoric acid to make the solution correspond to that of a steel containing about one per cent. of phosphorus. The yellow precipitate was shaken down from this, exactly in accordance with Dr. Dudley's method of phosphorus analysis. It was washed by decantation with ammonium sulphate, then with water, and finally dried to a constant weight at 130° C. This precipitate was found to be so hygroscopic that it was practically impossible to obtain accurate weights of it for analy-

sis. To avoid this difficulty, after carefully weighing it, the entire precipitate was dissolved in a slight excess of ammonium hydroxide, filtered through a balanced filter paper into a tared 200 cc. flask, the filter being washed with water until the 200 cc. mark was reached. The small amount of insoluble matter on the filter was determined after drying at 100° C., and the weight deducted from the original weight of the yellow precipitate. We now have a known weight of yellow precipitate in a known weight of solution, successive portions of which were weighed out from time to time for the determination of phosphorus and molybdic acid.

Phosphorus in Yellow Precipitate.—This was determined as follows: Accurately weigh off about twenty-five grams of solution, which is equivalent to about one gram of yellow precipitate, add ten cc. of magnesia mixture, stir well until precipitation begins, then add ammonium hydroxide to the amount of about one-third the bulk of the original solution, and allow to stand for several hours. Filter and wash with ammonium nitrate solution until free from chlorine, then ignite while moist. Purify the magnesium pyrophosphate by dissolving in dilute hydrochloric acid, filtering from any insoluble residue, and precipitating as before by the addition of ammonium hydroxide, five cc. of ammonium chloride solution, and five cc. of magnesia mixture. Allow to stand twelve hours, ignite and weigh.

The reagents used were made up as follows:

Ammonium chloride.—One part ammonium chloride to eight parts of water.

Magnesia mixture.—From magnesium chloride as per Chemical Analysis of Iron, p. 58, by A. A. Blair.

Ammonium hydroxide.—0.90 sp. gr.

Ammonium nitrate wash water.—One part ammonium hydroxide 0.90 sp. gr. to three parts water, then add two grams of ammonium nitrate for each 100 cc. of solution.

Molybdic Acid in Yellow Precipitate.—The method used for this determination was as follows: Weigh off accurately an amount of solution equivalent to about 0.25 gram of yellow precipitate, dilute with 150 cc. of water and bring to a boil. Neutralize the boiling solution with acetic acid, and add about five cc. in excess of the neutral point. Add at once twenty-five cc. of lead acetate,

or one cc. for every 0.01 gram of yellow precipitate present in the solution, and allow to digest an hour and a half at nearly a boiling temperature, in order to render the precipitate compact and granular. Filter on a Gooch crucible and wash with hot water about eight times by decantation. After the fifth or sixth washing the filtrate should give no reaction for lead when tested with ammonium sulphide. Dry to a constant weight at 130° C. This gives us the weight of $Pb_3(PO_4)_2 + PbMoO_4$. From the previous determination of phosphorus we now compute the $Pb_3(PO_4)_2$, and deduct this weight from that of the mixed precipitates. The difference gives us the weight of $PbMoO_4$, which multiplied by the factor 0.39237 equals molybdic acid (MoO_3).

The reagents used were made up as follows:

Lead Acetate.—Sixty grams crystallized salt in two liters of water, to which fifteen cc. of acetic acid were added.

Acetic Acid.—1.04 specific gravity.

Before using the above method for the determination of molybdic acid, we carefully investigated its merits and found it to be thoroughly reliable under all ordinary conditions of precipitation, the acidity, bulk and temperature of the solution having only a slight influence. On attempting to ignite the precipitate, however, as directed in the method as originally published in the *Ber. d. chem. Ges.*, 4, 280, we invariably found a loss varying from 0.2 per cent. to 3.0 per cent., and even more, according to the duration and intensity of ignition. But by drying on a Gooch crucible at 130° C. we obtained very constant results, which we believe to be in every way reliable.

The analysis of the yellow precipitate by the above methods gave us as follows: Phosphorus, 1.648 and 1.644 per cent., an average of 1.646 per cent.

Molybdic acid, 91.61, 91.59, 91.61 and 91.57 per cent., an average of 91.595 per cent. Our ratio between phosphorus and molybdic acid as computed on these analyses is 1.797.

We determined the molybdic acid in the filtrates from the phosphorus determinations and obtained 92.25 and 92.41 per cent. These results are higher than those previously obtained in the separate determinations, but as this difference was not sufficient to change to any extent our ratio we did not investigate the cause.

We now went a step further, in order to prove that the ratio between the phosphorus and molybdic acid in the yellow precipitate actually obtained in a steel analysis, is identically the same as that in the yellow precipitate shaken down from the prepared solution of phosphorus.

We separated a considerable amount of yellow precipitate from a steel containing 0.10 per cent. phosphorus, by Dr. Dudley's method of analysis, and after drying to a constant weight at 130° C. made the determinations of phosphorus and molybdic acid exactly as in the case of the previous precipitate, obtaining the following results: Phosphorus, 1.638 and 1.648 per cent., an average of 1.643 per cent. Molybdic acid, 91.63 and 91.67 per cent., an average of 91.65 per cent.

The ratio between phosphorus and molybdic acid given by these figures is 1.792, thus confirming our previous results and the generally accepted figure of 1.794.

From the work above outlined it would seem evident that the ratio of phosphorus to molybdic acid can be derived much more accurately from the analysis of the yellow precipitate than by the method suggested by Dr. Dudley.

The elaborate investigations of Hundeshagen (*Chem. News*, Oct. 4, 11, 18, 25, and Nov. 1, 1889,) have shown that ammonium phosphomolybdate is far more uniform when prepared under varying conditions than was formerly supposed. If the conditions of precipitation of the yellow precipitate are maintained constant, there is but little doubt as to its uniform composition. The ratio then becomes a question of the accuracy of the determinations of phosphorus and molybdic acid in the yellow precipitate. We have accordingly given the methods used for these determinations as completely as possible, in order to afford an opportunity for criticism and duplication.

Ratio between Iron and Molybdic Acid.—The ratio between phosphorus and molybdic acid being established, we then took up the ratio between iron and molybdic acid, as the investigations of Mr. Babbitt, *J. Anal. Appl. Chem.*, 7, 165, and our own experience had indicated that the commonly accepted ratio, 90.76, is too high where the reductor is used, the reduction being considerably greater than with the ordinary method of reducing with zinc powder and shot.

Our first experiments were on the standardization of a permanganate solution by the ordinary method of dissolving the steel in a flask in an atmosphere of carbon dioxide gas, as compared with the figure obtained when the steel was dissolved in an open beaker and reduced through the reductor. No appreciable difference was found, the reduction being complete in both cases.

We then made a large solution of molybdic acid of such a strength that fifty cc. contained 0.25 gram of the salt. The first experiments with this solution were made after the reductor had been in use some time, and the zinc was packed closely together, so that the solution encountered considerable resistance to its progress, and the acid had some time to act on the zinc, the result being that the reductor became quite hot. Upon cleaning out the reductor and filling with entirely fresh zinc, we were surprised to find our results very appreciably lower, no matter how slowly the solution was passed through the reductor, and only after heating the solution nearly to boiling did we obtain the results in the first case. This demonstrates that care must be taken to have the solutions hot when they are reduced, in order to obtain complete reduction, but with this precaution the results are very uniform, as will be seen from the table following. In each of the following experiments fifty cc. of the above mentioned molybdic acid solution was used.

Experiments with reductor:

RESULTS EXPRESSED IN CUBIC CENTIMETERS OF PERMANGANATE.

| REDUCTOR CLOGGED FROM
LONG USE. | | REDUCTOR CONTAINING FRESH
ZINC. | | |
|---|--|---|--|---|
| Five cc.
sulphuric
acid,
cubic
centimeters. | Ten cc.
sulphuric
acid,
cubic
centimeters. | Five cc.
sulphuric
acid,
cubic
centimeters. | Ten cc.
sulphuric
acid,
cubic
centimeters. | Five cc. sulphuric
acid solution
heated to 95° C.,
cubic
centimeters. |
| | 75.2 | 74.8 | 74.6 | |
| 75.25 | 75.3 | 75.0 | 74.7 | 75.45 |
| 75.35 | 75.4 | 74.9 | 74.7 | 75.35 |
| 75.45 | 75.3 | 74.95 | 74.8 | 75.35 |
| Average, 75.35 | 75.3 | 74.91 | 74.70 | 75.38 |

Our experience with the reductor has been that in order to secure complete reduction, it is necessary to have the column of zinc of considerable length, and to pass the solution through

very slowly. We would not feel safe in using a column of zinc less than ten inches in length. In reducing a solution which has a bulk of 200 cc. at least two minutes should be allowed for passing through.

Turning now to the reduction of molybdic acid by heating with zinc and sulphuric acid, we found that very different results could be obtained by the various modifications of the method. These methods vary not only in the amounts of zinc and sulphuric acid recommended, but also in the temperature used and the time of heating.

We experimented with the method given in Chemical Analysis of Iron, by A. A. Blair, p. 97. Fifty cc. of our stock molybdate solution reduced in this manner required 73.23 cc. of permanganate.

We then reduced the molybdic acid solution as follows: Fifty cc. of stock molybdic acid were measured off, twenty grams of zinc (and four large shot) were added, together with thirty cc. of ammonia (1:3). This was heated almost to boiling, eighty cc. of hot sulphuric acid (1:4) added, and allowed to reduce for fifteen minutes, keeping the solution at a gentle boil. Fifty cc. of the stock solution reduced in this manner gave as a mean of a number of determinations 74.2 cc. of permanganate.

It will be noticed that there is quite a difference between these results, and also that the highest value obtained by the zinc and sulphuric acid method is considerably lower than that given by the reductor. In some laboratories the zinc and sulphuric acid method of reduction is used with a less amount of zinc, shorter time, and at temperatures which do not reach the boiling point. In such cases the reduction is certainly far from complete.

The mean of four gravimetric determinations upon this same solution show the amount of molybdic acid contained in fifty cc. to be 0.233264 gram. The average number of cubic centimeters of permanganate used in titrating this amount after being passed through the reductor is 75.35, hence one cc. permanganate = 0.003096 molybdic acid. A careful standardization of the permanganate solution against iron gave its value as one cc. = 0.003472 gram iron, hence the ratio between iron and molybdic

acid, when the reduction is made by means of the reductor in our hands gives 89.16 instead of 90.76 as found by Mr. Emmerton. This difference is readily accounted for by the difference in the method of reducing the solutions. Our figure tends to corroborate the work of Mr. Babbitt in this connection although it does not correspond exactly with the one he obtained. From the foregoing work it would seem that the ratio between phosphorus and molybdic acid of 1.794 is correct, but that where the reductor is used 89.16 represents more nearly the correct ratio between iron and molybdic acid, hence our results are computed on this basis.

The Effect of Temperature on the Precipitation of Arsenic.—With the exception of these factors we found no fault with the method given by Dr. Dudley and the uniformity of the results obtained was very gratifying. To divide the errors liable to occur in weighing out the sample, and for convenience in manipulation, we have altered the method slightly in the direction of using a larger sample of steel and smaller bulk of solutions. A large number of determinations have proved that we do not in any way decrease the accuracy of our results by these changes. In detail, the method, as used by us, is as follows: Dissolve 1.5 grams steel in seventy-five cc. nitric acid 1.135 sp. gr. in an eight-ounce Erlenmeyer flask, allow to dissolve on the hot plate and boil hard for about one minute after the steel is in complete solution. Add crystals of potassium permanganate until a permanent purple color is obtained which will remain for at least one-half a minute on boiling. In order to secure such a color, enough permanganate must be added to form a copious dark brown precipitate of manganese dioxide. The crystals of permanganate must be added carefully to prevent the solution from boiling over. Remove the flask from the plate and add ferrous sulphate free from phosphorus, with constant shaking, until the solution clears. Cool to 38° C. and add seventy-five cc. molybdic acid at 27° C. Shake hard for five minutes, filter off the yellow precipitate and wash with ammonium sulphate wash water until the filtrate shows no reaction for molybdic acid when tested as previously described. Dissolve the precipitate in ammonia (1:3), using as little as possible. Wash the paper once with water, and pass the liquid back through the filter and wash

thoroughly. The bulk of this filtrate should not exceed 150 cc. Acidify with five cc. concentrated sulphuric acid, and reduce with the aid of the reductor, passing the liquid slowly through a ten-inch column of zinc. Titrate with potassium permanganate.

Our next step was to ascertain if the method or any modification of it could be used in the presence of arsenic without serious error from that source. Solutions of arsenic were made up by dissolving arsenious oxide in a small amount of a solution of sodium acid carbonate, and diluting with nitric acid 1.135 sp. gr. The strength of these solutions was so adjusted that seventy-five cc. of each would correspond to 0.1, 0.5, and 1 per cent. of arsenic when 1.5 grams of steel are used. Blank experiments were first made with the chemicals to be used, following in every detail the method given. The average of the results obtained are given in the table which follows. We then shook down in the same manner the three arsenic solutions prepared as stated, trying the effect of different temperatures, but were unable to bring down any appreciable amount of arsenic as the table will show.

| | Percentage of arsenic added. | Temperature of solution. | Temperature of molybdic acid. | Temperature of the mixture when shaken. | Result in terms of phosphorus, per cent. | Blank exper. on chemicals in terms of phosphorus, per cent. | Arsenic obtained in terms of phosphorus, per cent. |
|----------------------------|------------------------------|--------------------------|-------------------------------|---|--|---|--|
| Blank exper. | .. | 85° C. | 27° C. | 52° C. | | 0.0006 | |
| Blank exper. | .. | 16° | 16° | 16° | | 0.00034 | |
| Blank exper. plus arsenic. | 1 | 85° | 27° | 52° | 0.0023 | | 0.0017 |
| " | 1 | 16° | 16° | 16° | 0.0010 | | 0.0006 |
| " | 5 | 85° | 27° | 52° | 0.00085 | | 0.0051 |
| " | 5 | 16° | 16° | 16° | 0.0016 | | 0.0010 |
| " | 1 | 85° | 27° | 52° | 0.0018 | | 0.0012 |
| " | 1 | 16° | 16° | 16° | 0.0014 | | 0.0011 |
| " | 5 | 85° | 27° | 52° | 0.0014 | | 0.0011 |
| " | 1 | 16° | 16° | 16° | 0.0018 | | 0.0012 |
| " | 5 | 85° | 27° | 52° | 0.0018 | | 0.0012 |
| " | 1 | 16° | 16° | 16° | 0.0018 | | 0.0015 |
| " | 5 | 85° | 27° | 52° | 0.0018 | | 0.0015 |

These tabulated results gave us no little surprise, being so entirely contrary to the behavior usually attributed to arsenic. But we have repeatedly duplicated them, confirming our first results in every case. To investigate the matter still further we made a solution of pure nitrate of iron and phosphoric acid of such a strength that twenty cc. contained approximately 1.5 grams of iron and one-half per cent. of phosphorus. Analysis of

this solution, made as before and shaken down at 85° C., gave 0.442 per cent. phosphorus, duplicate 0.446 per cent. On the addition of 0.25 per cent. of arsenic to this solution and shaking down to 85° we obtained 0.484 per cent. phosphorus, duplicate 0.489 per cent., or an increase of 0.4 per cent., due to the arsenic added. We then took the four samples of steel on which our previous work had been done, and to each of these was added 0.1 per cent. of arsenic and the analysis shaken down with the results shown in the following table:

| | Arsenic added per cent. | Temperature of solution. | Temperature of molybdic acid. | Temperature of mixture when shaken. | Phosphorus obtained before arsenic was added. | Phosphorus obtained after arsenic was added. | Arsenic obtained in terms of phosphorus. |
|---------------------------------|-------------------------|--------------------------|-------------------------------|-------------------------------------|---|--|--|
| Iron salt plus phosphoric acid. | 0.25 | 85° C. | 27° C. | 52° C. | 0.442 | 0.484 | 0.042 |
| No. 27. | 0.10 | " | " | " | 0.110 | 0.119 | 0.009 |
| " 789. | 0.10 | " | " | " | 0.021 | 0.022 | 0.001 |
| " 344. | 0.10 | " | " | " | 0.066 | 0.067 | 0.001 |
| " 65. | 0.10 | " | " | " | 0.012 | 0.012 | 0.000 |

As the arsenic in these determinations was precipitated under identically the same conditions as were previously used in our blank experiments, except phosphorus being present, it is reasonable to infer that the action is a mechanical one, the ammonium phosphomolybdate carrying down with it a little of the arsenomolybdate, the amount depending largely upon the size of the precipitate. Our results given above tend to demonstrate this quite conclusively. We repeated the above work using Wood's formula for molybdic acid, shaking for ten minutes instead of five, allowing the precipitate to stand for fifteen minutes before filtering off, to ascertain if any of these variations had any influence on the precipitation of arsenic. We found that they made no appreciable difference in our results. If the method is followed as outlined, and the temperature of the solutions is not higher than that specified, so that the actual temperature at which the shaking takes place does not exceed 49° to 55° C., the error will never be appreciable, except in the case of a steel very high in both phosphorus and arsenic. One point, however, we have been unable to check up, and that is if arsenic which has been reduced from the ore with the iron behaves the same as

arsenic artificially introduced. We were wholly unable to obtain a sample of steel containing an appreciable amount of arsenic, upon which to work, and have been obliged to leave this until some future time when we may be fortunate enough to secure the necessary sample.¹ It is conceded by every one that temperature is an all-important factor in the precipitation of phosphorus in the presence of arsenic. We know that above a certain temperature arsenic is sure to come down in greater or less amounts. The question then arises, how high a temperature is necessary for the complete precipitation of phosphorus, or in other words, how low a temperature can we use and feel sure we have precipitated all the phosphorus. Numerous experiments upon various samples of steel at 32° and 55° temperature have shown that the results at 32° C. are slightly lower. This difference does not usually exceed 0.001 per cent. if precautions are taken to thoroughly shake the solution, and to use a paper sufficiently close to hold every trace of the fine precipitate. In view of the fact that the difference between the results obtained at the two different temperatures is so slight, and also that there is danger of contamination in the case of a steel high in both phosphorus and arsenic, we adopted the lower temperature.

It may be asked how do the results obtained by this volumetric method compare with those given by gravimetric methods of wide reputation, such as the acetate method. We regret that we were unable to make acetate determinations of the phosphorus in the four standard samples of steel previously used, but our investigations of the molybdate method proved so much more exhaustive, than we had anticipated, that these samples were used up in that work. However, we spent considerable time on a steel which had been examined by a number of well-known chemists. The results obtained by others are as follows:

| Acetate method. | | | | Molybdate method. | | | |
|-----------------------------|---|---|---|----------------------------|---|---|---|
| 0.047 per cent. phosphorus. | | | | 0.059 per cent phosphorus. | | | |
| 0.048 | " | " | " | 0.050 | " | " | " |
| 0.046 | " | " | " | 0.060 | " | " | " |
| 0.050 | " | " | " | | | | |

¹ Since writing the above we have received, through the kindness of Mr. W. P. Barba, of the Midvale Steel Company, a sample of steel said to contain 0.093 per cent. phosphorus, and approximately 0.12 per cent. arsenic. The average of a number of determinations on this sample, by the above method, gave 0.095 per cent. phosphorus—thus confirming what we had previously observed.

Our results on this sample were 0.048 by the acetate method and 0.055 by the volumetric. By the combination method described above, which seems to exclude many of the chances of error which occur in either the acetate or molybdate method, we found 0.0538 per cent. phosphorus.

It will be noticed that the results obtained by the acetate method are lower than either of the others. This has been our experience repeatedly, when we have compared the three methods, the acetate giving invariably the lowest results.

We will not enter into a discussion in regard to the causes for this as they are many, and this is not the purpose of our paper, but in our opinion the proposed Committee on Standard Methods can do no greater benefit to the iron industry of our country than by a thorough investigation of the methods used for the determination of phosphorus in ores and finished products. From our personal observation we know that frequently injustice is done, and able chemists brought into disrepute, simply because their results have not agreed with those obtained by analytical chemists of wide reputation, whose methods have not told the whole truth.

ON THE QUALITATIVE DETERMINATION OF TANNING MATERIALS.¹

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It can hardly be said that any systematic attempt has been made to formulate a scheme for distinguishing the various tanning materials by their qualitative reactions, except perhaps a very slight table published by the writer, although, in view of the constantly increasing number of new tanning materials, and especially of new extracts which are offered to tanners, the matter has become one of considerable practical importance. The commercial value of an extract is dependent, not only on the percentage of tanning matter as determined by analysis, but on the nature of the tannin present, which influences the character of the leather produced.

It is, of course obvious, that, failing a clear knowledge of the

¹ Read before the World's Congress of Chemists, August 25, 1893. Proof of this article was kindly read by Professor Henry Trimble.

tannins themselves any definite scheme of separation is for the present impossible; since, although we have good reason to believe that the tannins are a class, we are quite ignorant of their number, which may easily be a comparatively small one, as many members of the group which at present receive individual names are probably mere mixtures. What can be done is to separate the tanning materials into groups or individuals by reactions which have been empirically determined; of which in many cases we do not know the chemical significance, and which may possibly be often due to other constituents of the materials than the tannins themselves. The question is still further complicated by the fact that woods, barks, and fruit of the same tree often yield tannins of distinctly different character. In view of these facts, the group tables given must be only regarded as pointing out the general character of the material examined, and their indications must always be confirmed by direct comparison of *all* the reactions observed with those given by the material suspected. It must also be remembered that in some cases the group reactions are uncertain, or may be simulated by mixtures, which may often be determined by comparison of the results of the more special tests.

In this connection it may be noted that most of the reactions under the intermediate groups might be simulated by suitable mixtures of A and F; and that the inconstancy of the iron reaction in closely allied trees, points either to their containing mixtures of tannins, or to the existence of a very large number of closely allied tannins of very similar constitution. The point is one very difficult of decision, since we have no really reliable method for separating different members of the family.

It was thought that some information as to the meaning of the reactions employed might be obtained by examining the behavior of the simpler derivatives under the same circumstances, and the results are given in table X. It will be at once obvious that the blue-black reaction with iron is characteristic of the pyrogallol group; and the green-black equally so of the catechol derivatives, while phloroglucol, contrary to the statements of the text-books, gives no marked reaction with iron, but is alone characterized by the very delicate reaction

with the vanillin present in deal. On the remaining reactions little light is thrown.

In qualitative work with tanning materials, a good deal depends on the strength of the solutions, and the way in which the tests are performed, and as the information in the Tables is necessarily very brief, a few preliminary words are desirable.

Infusions of tanning materials are understood to be of about the strength used by the writer in determinations by hide-powder, *viz.*, about 0.6 gram of dry soluble matter in 100 cc., but moderate divergencies from this do not influence results. Of course where reactions are feeble in any case, with very dilute solutions they may be imperceptible, and on the other hand, strong solutions will sometimes give precipitates where only colorations are noted with weak ones.

Bromine water reaction.—It is best to add the bromine water drop by drop to 2–3 cc. of the infusion in a test tube, until the solution smells strongly. In some cases the precipitate is slight, or forms slowly, and occasionally it is crystalline and on this account less conspicuous, but it is usually a distinct yellow or brown flocculent one. In most cases bromine precipitates such tannins as give a green-black with iron, and in general terms it may be said to be a reagent for the catechol tannins.

Nitrous acid reaction.—This reaction, which is believed to be a new one, is obtained by adding to a few cc. of the infusion in a porcelain basin a distinct excess of solution of sodium or potassium nitrite, and then 3–5 drops of decinormal sulphuric or hydrochloric acid. In typical cases the solution instantly turns pink or crimson, and slowly changes through purple to a deep indigo-blue, but in others, as sumach where the reaction is feeble, and masked by other changes, the final color is green or even brownish. In a large number of cases, nitrous acid produces a yellow or brown coloration or precipitate, but "reaction" in the Tables invariably means a series of color-changes as above described. Nothing can as yet be said on the nature of the chemical changes produced. The reaction is given by all tanning materials which yield ellagic acid or "bloom," but not by ellagic acid itself, nor by pure gallotannic acid. It is possibly a reaction of ellagitannic acid.

Ferric alum, Ammonio-ferric sulphate.—A one per cent. solution of this salt has been chosen as easily obtainable, neutral, and in a state of approximate purity. Ferric chloride, which is generally used, is almost invariably strongly acid, and of a very persistent yellow. Acid ferric chloride in excess will give a green-black reaction with gallotannic acid itself, and its results as a test are often very misleading. Ferric acetate, which has also been largely used gives heavy precipitates with most materials and is very strongly colored, so that it was found less convenient than the iron alum. As the colorations are generally very powerful, they are best seen by diluting the tannin infusion freely, and adding the iron solution very cautiously. In many cases the coloration first produced, and which is the characteristic one, rapidly fades to a dull olive or brown in presence of excess of iron, probably by oxidation and destruction of the tannin.

Cupric sulphate and ammonia.—When solution of cupric sulphate is added to a tanning material infusion, it sometimes gives a precipitate, and sometimes not. This is a useful indication in some cases, but must not be regarded as of first rate importance as the presence of any weak organic salt would in all cases cause a precipitate, by neutralizing the sulphuric acid of the sulphate. Cupric acetate produces a precipitate with all tannins so far as I have observed, and it is interesting to note that in this case, as in many others of a like character, the tannin combines with, and precipitates the salt as a whole. On the addition of ammonium carbonate, effervescence takes place, and the precipitate darkens, and becomes a true tannate.

When ammonia is added to the mixture of a tannin and cupric sulphate, a precipitate is invariably formed in the first instance, consisting of a tannate of copper with variable quantities of blue cupric hydroxide. With excess of ammonia, the whole of this precipitate is in many cases dissolved, while in others, an insoluble tannate remains. The latter is the case with all tannins derived from gallotannic acid and with many containing protocatechuic acid and forms a useful means of classification, though as yet the difference of structure to which it corresponds is unknown. The fact that hemlock and other

pine barks, as well as cutch and gambier, yield cupric tannates soluble in ammonia is an instructive commentary on processes which have been proposed for quantitative estimation by precipitations by ammonio-cupric solutions.

Where the precipitate redissolves it generally does so with the production of either a greenish brown, or a purplish brown coloration, which in presence of a small amount of the blue ammonio-cupric sulphate, appears either as a green or a reddish violet, and is again a useful means of identification. It need hardly be pointed out that to see this coloration well, the copper should be in the least possible excess. Hence it is desirable to use a very weak copper solution, say at most one per cent.

Stannous chloride and hydrochloric acid.—This reagent, the application of which is here first published, consists in a strong solution of stannous chloride in concentrated hydrochloric acid. If about ten cc. of this are added to one cc. of the tanning material infusion, in a porcelain basin, and allowed to stand for ten minutes, coniferous tans, mimosas, and some others give a very marked pink coloration. This is specially distinct in the case of larch bark. If a small piece of larch-tanned leather be steeped in the reagent, the coloration appears very strongly.

Deal shaving and Hydrochloric acid.—A shaving or slip of any pine wood is moistened with the infusion, and then, either before or after drying, is again moistened with concentrated hydrochloric acid. In the case of cutch and gambier, and a few other materials, the spot becomes at once a bright red or violet, but in many cases the reaction is faint, and only appears after some hours. It probably always indicates the presence of phloroglucol.

Sodium Sulphite—This was mentioned in my previous manuscript on the subject, but the printer unfortunately substituted sodium sulphide, which does not answer in the laboratory.

In some cases these reactions will serve to determine the constituents of mixtures but in many cases this will continue impossible till further and more distinctive reactions are discovered.

They can of course be applied to the recognition of tannates, when excess is present in leather which can be dissolved out

with water; but the effect of dilute alkalies and other solvents on the reactions is worth further experiment.

A few drops of the solution are placed in contact with a crystal of sulphite on a tile or in a basin. With valonia, a bright purplish pink is rapidly developed, apparently by oxidation. Many other tanning materials produce red or pink colorations, but in no case so marked a reaction as valonia.

Concentrated sulphuric acid.—A test tube is rinsed out with the infusion, and drained so that only about a drop remains, and concentrated acid is cautiously poured into the sloping tube, so as to form a layer underneath the tannin solution. The ring of color at the junction of the two liquids is noted, and then they are mixed by shaking, and diluted with water. About half the materials give a deep purplish crimson, called simply "crimson" in the Tables, and in many cases this is decidedly pink on dilution, while in other cases it is obscured by brown products formed by the heat of mixture. A large number of other materials give browns or yellows only, which when intense appear red, but dilute to yellows or yellow-browns.

Lime water is a most useful reagent, being very varied in the color of the precipitates it produces, and the changes they undergo by oxidation. The reaction is best seen in a shallow porcelain basin.

QUALITATIVE CLASSIFICATION OF TANNING MATERIALS. TABLE I.

| Bromine water produces a precipitate. | | | Bromine water produces no precipitate. | | |
|---|---|------------------------|---|--|--|
| Nitrous acid gives no reaction or merely darkens. | Nitrous acid causes a red coloration, becoming violet and blue or green. | | Nitrous acid gives no reaction or merely darkens. | Nitrous acid produces a red coloration changing to violet and blue or green. | |
| | Iron alum blue-black. | Iron alum green-black. | | Iron alum blue-black. | Iron alum green-black. |
| Copper sulphate followed by ammonia in excess. | Group B. Table V. | Group C. Table VI. | Group D. Table VII. | Group E. No members of this group known but <i>radic acid</i> and <i>protocatechuic acid</i> , which are not tannins. See Table X. | Group F. Table VIII. |
| | Precipitate is insoluble in excess of ammonia-Group A γ . Table IV. | | | | Group G. No members of this group known. |
| | Precipitate redissolves with green or olive brown coloration-Group A β . Table III. | | | | |
| | Precipitate redissolves with reddish violet coloration-Group A α . Table II. | | | | Group H. Table IX. |

TABLE II.

| Group A a. | Ferric alum. | Bromine water. | Nitrous acid. | CuSO ₄ + NH ₄ OH | SnCl ₂ + HCl. | Deal shaving and HCl. | Na ₂ SO ₃ . | H ₂ SO ₄ . | Lime water. |
|---|-------------------------|----------------|------------------------|---|--------------------------|-----------------------|-----------------------------------|----------------------------------|----------------------------|
| Cutch from <i>Ac. catechu</i> wood. | Green-black. | pp. | No react. darkens. | pp. redissolves generally red-violet c'l'n. | No react. | Deep violet-red. | Reddens somewhat. | Red-brown coloration. | Reddish pp. slowly formed. |
| "Thaun leaf" extract (<i>a cutch substitute</i>). | Olive-black pp. | pp. | No react. darkens. | pp. redissolves brownish coloration. | No react. | No react. | No react. | Crimson, pink on dilution. | No pp. |
| "Turwar" bark. (<i>Cassia auriculata</i> .) | Green-black. | pp. | No react. darkens. | pp. redissolves red-violet. | No react. | Trace. | Pink coloration. | Crimson. | Reddish pp. |
| "Gambene" extract (<i>a gambier substitute</i>). | Green-black coloration. | pp. | No react. darkens. | pp. redissolves red-violet. | No react. | No react. | Slight pink coloration. | Crimson-pink diluted. | Reddish pp. |
| "Tengah" bark (<i>Crotons Candolleana</i>). | Green-black coloration. | pp. | No react. darkens. pp. | pp. redissolves red-violet. | Pink coloration. | No react. | Pink coloration. | Crimson. | Bright red pp. |
| Bark (<i>Acacia leucophloea</i>). | Green-black coloration. | pp. | No react. | pp. redissolves red-violet. | Pink coloration. | Slow violet react. | Pink coloration. | Crimson-pink diluted. | Dull brown pp. |

TABLE III.

| Group A. β . | Ferric alum. | Bromine water. | Nitrous acid. | $\text{CuSO}_4 + \text{NH}_4\text{OH}$. | $\text{SnCl}_2 + \text{HCl}$. | Deal Shaving and HCl . | Na_2SO_3 . | H_2SO_4 . | Lime water. |
|---|-------------------------|----------------|-------------------------------------|--|--------------------------------|---------------------------------|----------------------------|---------------------------|-------------------|
| Gambier. (ext. of leaves of <i>Nauclea gambier</i>). | Deep green coloration. | pp. | No react. darkens | pp. redissolves olive-green. | Yellow. | Deep violet-red. | Yellow. | Crimson dilutes brown. | No pp. |
| (1) "Purim Bast." (leaves of <i>Colpoon</i> or <i>Oxyris compressa</i>). | Green-black. | pp. | No react. | No pp. redissolves green. | No react. | Pink. | Yellow. | Crimson dilutes brown. | Light yellow pp. |
| (2) "Koko" natal. (leaves of <i>Crataegus buxifolia</i> .) | Green-black. | pp. | No react. | No pp. redissolves green. | No react. | No react. | Yellow. | Dark brown. | Bright yellow pp. |
| Larch bark (<i>Larix Europaea</i>). | Green-black coloration. | pp. | No react. darkens. | pp. redissolves olive-green. | Pink coloration. | No react. | No react. darkens. | Deep red-brown. | Rusty pp. |
| Hemlock bark (<i>Tsuga</i> or <i>Abies Canadensis</i> .) | Olive-green reddish pp. | pp. | No react. pink with NaNO_2 | pp. redissolves neutral tint. | Pink coloration. | No react. | Reddens. | Crimson dilutes pinkish. | Red-brown pp. |
| "Larch" extract (<i>Abies extelae</i>). (§) | Green-black or brown. | pp. | No react. | pp. redissolves olive-green coloration. | Pink coloration. | No react. | Darkens. | Deep red-brown. | Brown pp. |

(1) Used at Cape of Good Hope as sumach.

(2) Used in Natal as sumach substitute.

(3) *Fichte*, *Rothanne* Norway or common spruce. *Abies pectinata* the *Weiss* or *Edel-Tanne* or silver fir is said to give a blue-black with iron.

TABLE IV.

| Group A γ. | Ferric alum. | Bromine water. | Nitrous acid. | CuSO ₄ , NH ₄ OH. | SnCl ₂ , HCl. | Deal shaving and HCl. | Na ₂ SO ₃ . | H ₂ SO ₄ . | Lime water. |
|--|-------------------------|----------------|-------------------|---|--------------------------|-----------------------|-----------------------------------|----------------------------------|-----------------------------|
| Willow bark.
(Russian. Sp. unknown.) | Green-black. | pp. | No react. | Slight pp.
Dense pp. | No react. | Violet faint. | Pink coloration. | Red-brown not intense. | Slight greyish pp. |
| <i>Acacia Anglica</i> or
<i>Pyralidica macrocarpa</i> . | Green-black. | pp. | No react. | Slight pp.
Dense choice pp. | Pink or violet color. | Violet faint. | Reddus somewhat. | Crimson dilutes pink. | Reddish pp. |
| <i>Acacia rattachi</i> bark. | Green-black. | pp. | No react. | No pp.
Dense violet-black pp. | Possible trace. | Trace. | Pink color. | Red-brown. | Flesh color pp. |
| "Thorn tree" bark.
(<i>Acacia horrida</i>) (Cape.) | Green-black. | pp. | No react darkens. | No pp.
Dense pp. | No react. | Doubtful. | Pink color. | Dull crimson not intense. | No pp. |
| Mangrove bark extract.
(<i>Rhizophora mangk.</i>) | Green-black. | pp. | No react. | No pp.
Reddish-black. | Slight reddening. | No react. | Slight reddening. | Red-brown. | Red pp. darkened by excess. |
| Quebracho wood extract.
(<i>Loxopterygium Lorentzii</i> .) | Green-black coloration. | pp. | No react. | Slight pp.
Dense pp. | Pink color pp. | Trace. | Doubtful. | Crimson coloration dilutes pink. | Light brown pp. |
| "Sugar brush" bark. (Cape.)
(<i>Protea mellifera</i> .) | Green-black. | pp. | No react darkens. | No pp.
Dense pp. | No react. | Trace. | Doubtful. | Red. | Yellow-brown pp. |
| "Waagenboom" (Cape.)
(<i>Protea grandiflora</i> .) | Green-black. | pp. | No react darkens. | No pp.
Dense pp. | No react. | Trace. | Pink color. | Crimson dilutes pink. | Light yellow pp. |
| "Kruppelboom" (Cape.)
(<i>Leucospermum conocarpum</i> .) | Green-black. | pp. | No react darkens. | No pp.
Dense pp. | No react. | Violet distinct. | Pink color. | Crimson dilutes pink. | Slight greyish pp. |
| "Silver tree" (Cape.)
(<i>Leucodendron argentea</i> .) | Green-black. | pp. | No react darkens. | No pp.
Dense pp. | No react. | No react. | Pink coloration. | Crimson dilutes pink. | Flesh color pp. |

TABLE V.

| Group B. | Ferric alum. | Bromine water. | Nitrous acid. | CuSO ₄ + NH ₄ OH. | SnCl ₂ + HCl. | Deal shaving and HCl. | Na ₂ SO ₄ . | H ₂ SO ₄ . | Lime water. |
|--|------------------|-------------------------|-----------------------|--|--------------------------|-----------------------|-----------------------------------|----------------------------------|-----------------------------|
| "Skens," Cypress Sumach
(possibly <i>Cotaria myrtifolia</i>). | Blue-black pp. | pp. | No react. | Slight pp.
Dark pp. | No react. | No react. | Yellow. | Yellow-brown. | Yellow pp.
dark'ning |
| Klipfont bark (1)
(<i>Rhus Thunbergii</i>). | Blue-black. | pp. | No react. | No pp.
Dense dark pp. | No react. | No react. | Pink. | Dull crimson dilutes orange. | Pinkish pp. |
| Canaigre
(Root of <i>Rumex hymenosepalus</i>). | Blue-black pp. | pp. | No react. | Slight pp.
Dense dark pp. | No react.
clouds. | Trace violet. | Slight dark'ning | Yellow-brown. | Pink coloration greyish pp. |
| "Talwan" or "Elandsbortjes"
(Root <i>Elephantorrhiza Hurchellii</i>). | Blue-black pp. | pp. | No react.
darkens. | Slight pp.
Dense dark pp. | No react. | Trace violet. | Pink. | Red. | Reddish brown pp. |
| Mimosa or Wattle bark
(Various Austral. Acacias). | Dirty violet pp. | pp. | No react. | Slight or no pp.
Dense purple brown pp. | Slight reddening | Sometim's trace. | Reddens. | Crimson dilutes pink. | Reddish or yellow-brown pp. |
| Babool bark. India.
(<i>Acacia Arabica</i>). | Dirty violet pp. | pp. | No react. | Slight or no pp.
Dense dark pp. | Some trace. | Faint trace. | Slight dark'ning | Crimson dilutes orange. | Dark reddish brown pp. |
| Dark red Austr. bark
(Probably an acacia). | Dirty violet pp. | pp.
needle crystals. | No react. | Slight pp.
Deep violet pp. | No react. | Faint trace. | Orange-pink. | Crimson dilutes pink. | Bright violet pp. |
| "White bark" <i>Algaroba blanca</i>
South America
(<i>A. prosopis</i> or <i>acacia</i>). | Dirty violet pp. | pp. | No react. | No pp.
Reddish black pp. | No react. | Violet. | Reddens strongly. | Crimson dilutes pink. | Red pp.
turning violet. |

(1) Used at Cape of Good Hope.

TABLE VI.

| Group C. | Ferric alum. | Bromine water. | Nitrous acid. | CuSO ₄ and ammonia. | SuCl ₂ + HCl. | Deal shaving and HCl. | Na ₂ SO ₃ . | H ₂ SO ₄ . | Lime water. |
|--|------------------------|----------------|---------------------------|--------------------------------|--------------------------|-----------------------|-----------------------------------|----------------------------------|--|
| Cork bark (<i>Quercus suber</i>). | Green-black coloration | pp. | Reacts somewhat. | Slight pp. — Brown color. | No react. | No react. | Reddens. | Crimson dilutes pink. | Reddish brown pp. |
| Green Oak (Ital.) (<i>Quercus ilex</i>). | Green-black coloration | pp. | Reacts faintly if at all. | Slight pp. — Brown color. | No react. | No react. | Reddens. | Crimson dilutes pink. | Reddish brown pp. |
| Garouille, Root Bark of Kernea Oak (<i>Quercus Coccifera</i>). | Green-black coloration | pp. | Reacts | Slight pp. — Brown color. | No react. | No react. | Reddens. | Crimson dilutes pink. | Reddish brown pp. |
| Quercitron Bark (<i>Quercus Tinctoria</i>). | Green-black coloration | pp. | Reacts somewhat. | Slight pp. — Brown color. | No react. Light green. | No react. | Doubtful. | Crimson dilutes pink. | Dyes yellow low with Sn. mordants. |
| Chestnut Oak (<i>Quercus Castanea</i>). | Olive-green coloration | pp. | Reacts distinctly. | Decided pp. Insol. in excess. | No react. | No react. | Reddens. | Crimson dilutes pinkish. | Infusions fluoresce especially with ammonia. |

TABLE VII.

| Group D. | Ferric alum. | Bromine water. | Nitrous acid. | CuSO ₄ and ammonia. | SuCl ₂ + HCl. | Deal shaving and HCl. | Na ₂ SO ₃ . | H ₂ SO ₄ . | Lime water. |
|---|---------------------------------|----------------|------------------|--------------------------------|--------------------------|-----------------------|-----------------------------------|----------------------------------|--|
| English Oak (<i>Quercus Robur</i>). | Blue-black (green with excess). | pp. | Reacts somewhat. | Slight pp. — Dark brown pp. | No react. | Paint react. | Reddens. | Crimson dilutes pink. | Reddish brown pp. |
| Jaft or Delict. (1) Supposed oak product. | Blue-black pp. | pp. | Reacts red-blue. | Brown pp. — Dark brown pp. | No react. Dark brown pp. | Paint react. | Some dark'ning | Crimson dilutes pink. | Strong infusions, dry whitish and infuscent. |

(1) A Persian product, dark scales very rich in tannin (about forty per cent).

TABLE VIII.

| Group F. | Ferric alum. | Bromine water. | Nitrous acid. | CuSO ₄ + NH ₄ OH | SnCl ₂ + HCl | Deal shaving and HCl | Na ₂ SO ₃ | H ₂ SO ₄ | Lime water. |
|--|----------------|---------------------|----------------------|--|-------------------------|----------------------|---------------------------------|--------------------------------|---|
| Aleppo galls
(of <i>Quercus infectoria</i>). | Blue-black pp. | No pp. slight acum. | Reacts red to blue. | G'nish pp. ———
Dark pp. insoluble. | Light yellow pp. | No react. | No react. | Greenish to dirty yellow. | Fale pp. turning bluish-green. |
| Sumach
(leaf of <i>Rhus coriaria</i>). | Blue-black pp. | No pp. | Reacts feebly. | G'nish pp. ———
D'k brown insol. pp. | No react. | No react. | No react. | Yellow. | Yellow pp. turning bright green. |
| Myrobalans
(<i>Tormentilla chebula</i>). | Blue-black pp. | No pp. | Reacts red to blue. | Yellow pp. ———
Dark in- soluble pp. | No react. | No react. | Yellow. | Yellow. | Yellow pp. turning greenish. |
| Pomegranate rind
(<i>Punica granatum</i>). | Blue-black pp. | No pp. | Reacts red to blue. | Brown pp. ———
D'k brown insol. pp. | No react. | No react. | No react. | Orange-brown. | Bright yellow pp. turning red with exc'as |
| Algarobilla (pod of
<i>Cassipouia brevifolia</i>). | Blue-black pp. | No pp. | Reacts red to blue. | S'ht g'n pp. ———
Dense dark pp. | No react. | No react. | Deep yellow. | Deep yellow-brown. | Bright yellow pp. darkens somewhat. |
| Divi-divi (pod of
<i>Cassipouia coriaria</i>). | Blue-black pp. | No pp. | Reacts red to blue. | S'ht g'n pp. ———
Dense dark pp. | No react. | No react. | No react. | Crimson. | Yellow pp. turning red-purple. |
| Algarobo (probably
pod of <i>Prosopis dulcis</i>). | Blue-black pp. | No pp. | Reacts red to olive. | S'ht g'n pp. ———
Dense dark pp. | No react. | No react. | Yellow. | Yellow to olive. | Yellow pp. turning black. |
| Valonia (Cup of
<i>Quercus Agalops</i>). | Blue-black pp. | No pp. | Reacts red to blue. | No pp. ———
Dark reddish pp. | No react. | No react. | Purplish pink. | Deep yellow. | Yellow pp. turning at purple. |
| "Oak wood" extract
(oak or chestnut wood). | Blue-black pp. | No pp. | Reacts red to blue. | Fale pp. ———
Purple brown pp. | No react. | No react. | Reddens. | Yellow-brown. | Yellow pp. turning red-purple. |

(1) Moderately strong potassium nitrite solution precipitates divi, but not *divi* oak wood solutions; pp. soluble in hot, or much cold water.(2) *Crude* chestnut wood extract may be distinguished from oak wood by its violet-reaction with ammonium sulphide (see "Graber" No. 261, p. 157).

TABLE IX.

| Group H. | Ferric alum. | Bromine water. | Nitrous acid. | CuSO ₄ and ammonia. | SnCl ₂ and HCl. | Deal shaving and HCl. | Na ₂ SO ₄ . | H ₂ SO ₄ . | Lime water. |
|---|----------------|----------------|--------------------|-----------------------------------|----------------------------|-----------------------|-----------------------------------|----------------------------------|------------------------|
| Pure Gallotannic Acid. | Blue-black pp. | No pp. | No react. | No pp. —
Dark pp. | No react. | No react. | No react. | Yellow. | Pale pp. turning blue. |
| Babool Pods.
<i>Acacia Arabica</i> . | Blue-black. | No pp. | No react. darkens. | Slight pp. —
Dark green color. | No react. | Faint violet. | No react. | Reddish violet. | Pink color. No pp. |

TABLE X.

| | Ferric alum. | Bromine water. | Nitrous acid. | CuSO ₄ and ammonia. | SnCl ₂ and HCl. | Deal shaving and HCl. | Na ₂ SO ₄ . | H ₂ SO ₄ . | Lime water. |
|--------------------|-------------------------------------|-----------------|--------------------|--------------------------------|----------------------------|------------------------|-----------------------------------|----------------------------------|--|
| Catechol. | Dark green coloration. | No pp. | Turns yellow. | No pp. —
Green color. | No react. | No react. | No react. | Green coloration. | No pp. |
| Pyrocatechuic acid | Dark green coloration. | No pp. | Turns brown. | No pp. —
No pp. | No react. | No react. | No react. | No react. | No pp. |
| Phloroglucol. | No react. | Bulky white pp. | Turns olive-green. | No pp. —
No pp. | No react. | Red-violet coloration. | No react. | Slight yellow. | No pp. |
| Pyrogallol. | Blue-black turning green and brown. | No pp. | Turns yellow. | No pp. —
Brown color. | No react. | No react. | No react. | Brown coloration. | Violet coloration rapidly turning brown. |
| Galic acid. | Blue-black coloration. | No pp. | Turns brown. | No pp. —
Brown color. | No react. | No react. | No react. | No react. | White pp. rapidly turning blue. |

THE IMPORTANCE OF THE STUDY OF BIOCHEMISTRY.¹

By E. A. DE SCHWEINITZ, WASHINGTON, D. C.

WHEN the controversy between the two schools of the vitalists and chemists as to the true cause of the diseases produced in animals by the inoculation of putrefactive organic matter was at its height, Panum, of Denmark, made some careful researches and extracted from putrid organic matter chemical substances, which, when perfectly free from every form of germ life, produced intoxication and death. But, he said the poison extracted from this putrid matter is undoubtedly a pure chemical compound, it may, however, be produced by a microbe, and both microbe and poison play their part in the disease.

Now more than fifty years later, though the microbial origin of most diseases has been thoroughly established, it has also been shown that the chemical products of these germs are the direct cause, in most instances, of the fatal effects. For example, in diphtheria the growth of the germ is but a local manifestation, while the poison it produces is distributed through the whole system. When, however, the germ has been discovered that is responsible for a disease or for other changes, to which we will presently refer, the door has but been opened for a study of the most interesting chemical problems that can be imagined. Germs in general are cells of protoplasm, and it is by a study of their actions and the changes which they produce that we can gain a better insight into the processes of life. Fortunately the majority of germs can be easily cultivated artificially, so that it is not difficult to obtain solutions of their products, but it is difficult to isolate these products from the solution and determine their nature. For the most part the substances produced by bacterial growth have been found to belong to two classes, the albuminoids and ptomaines, the latter corresponding closely in many of their properties and composition to the vegetable alkaloids. Our knowledge of the albuminoids, however, is very meager. We can divide them into certain general classes as 1, globulins; 2, albumoses (hemi-proteo or deutero albumoses),; 3, alkali or acid albumen; 4, peptones, etc.; but with this we have only made a step in the dark as it has given no idea of the actual

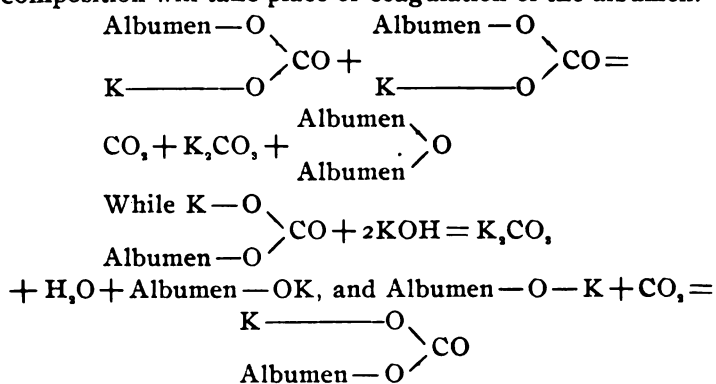
¹ Read at the Baltimore meeting, December 28, 1893.

composition of the substances about which we speak, beyond that they contain carbon, hydrogen, oxygen, nitrogen, and sulphur, and phosphorus in certain proportions, and differ in coagulation. Do these apparent albuminoid substances from bacteria belong to the class of albumoses, or are they chemical diastases or ferments, many of the reactions of which they show? Can they be proved to be diastases by their hydrating and digesting action and shown to be allied to ptyalin, pepsin, etc.? At first it was held, and is still held by some, that the presence of albuminoid matter was necessary to the growth of the germ and that the products of the germ life were changes or simply decomposition products of the albuminoid matter upon which they fed. But it has been proven too that some of the same substances are obtained by the simple action of acids and alkalies upon albuminoids, and it is often difficult to decide whether the albumoses and alkaloids have been produced by the germs or by the alkali or acid. To decide this it is necessary to cultivate the germs upon solutions which do not contain a trace of albuminoid matter. This Fermi and Uschinsky have succeeded in doing with a number of different germs upon a solution of glycerine and mineral salts (ammonium phosphate, and acid potassium phosphate), and I have also with the hog cholera, glanders, and recently tubercle bacillus by the addition of asparagine to the above liquid. From these cultures albuminoid substances have been obtained as well as alkaloids, showing that they have truly been built up and elaborated by the germ and are to be compared to intercellular secretions and excretions of these minute forms of life, and not to simple products of decomposition from albuminoid matter in solution. That the products formed under the different conditions are similar is shown by the same physiological action of mallein prepared from these artificial cultures or from cultures upon beef broth. This power of the germ to multiply upon a solution of mineral salts where the carbon, hydrogen, nitrogen, and phosphorus are present in an easily assimilable form is not surprising, for we deal here with the lowest form of vegetable life, and it is well known that plants cannot live upon albuminoid matter directly, but only when by decomposition it has been reduced to its elementary condition.

The study of these products of the germ life has made but little progress so far as their actual chemical constitution is concerned. Much more attention has been paid to their physiological effect. It has been learned that some of these products will render an animal insusceptible to the action of disease germs, but what the chemical change which can have taken place and caused this immunity may be, is one of the problems for the biochemist and physiologist to decide.

It has been found too that the blood serum of animals that have been made immune to disease has a germicidal action and will render other animals immune. Where does this property lie? What chemical change again has the blood undergone?

In his studies upon the albuminoids of the egg, Scholl has indicated where this property may be. He found that egg albumen exerted a germicidal effect, that this germicidal power was destroyed by heat and could be restored by treating the albumen with alkali. This was similar to some of Buchner's observations upon blood serum, where he found the bactericidal property could be restored by the use of an alkali. Scholl's theory for explaining this, and also at the same time the coagulation of albumen, is that the normal albumen has a composition corresponding to a bicarbonate, that upon heating, carbon dioxide is given off and the albumen coagulated by the consolidation of two molecules, while when the alkali albumen is heated no decomposition will take place or coagulation of the albumen.



The carbon dioxide in the albumen is also set free by acid in the

cold which will explain the coagulation of albumen by acid. In the albumen molecule then, there is a group of atoms with a bactericidal action, which grouping is destroyed by heat and restored by alkali, just as there are certain groupings necessary for the production of a disinfectant, or rather just as the disinfectants are characterized by certain groups. The confirmation of these experiments will open up a field of enormous possibilities, as sulphur is an element which in many cases can replace oxygen, and the resulting compounds would be very interesting, as well as lead to a number of new products and eventually to a better understanding of the albuminoid molecule.

As just mentioned, it has been found that in the case of a great many diseases, animals can be made insusceptible by vaccination, and that the blood of such immune animals will make others immune. But this immunity only holds for the particular disease against which the animal was first vaccinated, and does not protect the animal against another disease. A guinea pig can be protected from a hog cholera inoculation by an injection of the albuminoid product extracted from the cultures. The same pig will die if inoculated with swine plague. If, however, it be vaccinated both for hog cholera and swine plague, with the products extracted from their respective cultures, the animal will be insusceptible to both diseases. Just in the same way in each particular disease some chemical change is produced in the blood or tissues and the work of the chemist should be to find out what these changes are. The possibilities are enormous, the difficulties many, but by careful study, accompanied necessarily with a certain amount of bacteriological work and the observation of pathological changes, we can hope to arrive at a more definite understanding of the process of life.

It is, however, not only with reference to diseases that a study of biochemistry is important. From a practical and commercial standpoint the work is useful. J. A. Davalos, of Havana,¹ describes the isolation of a distinct ferment and a number of bacilli from different tobacco leaves, some of which in artificial culture give distinct poisons. The different varieties of tobacco show different germs. These germs, by their growth upon the

¹ *Cronico Medico-quirurgica de la Habana*, 1892. No. 15.

tobacco, give to it its peculiar flavor and odor, and the different qualities of tobacco owe their value to some particular ferment. As I have noticed, a bright yellow American high grade tobacco shows the presence of a germ altogether different, producing different substances from that of a low grade tobacco. Therefore, if the germs of a low grade tobacco can be destroyed and those from a fine tobacco substituted, we should be able to greatly improve the manufactured article. Now in practice, before the fermentation, some good tobacco is often mixed with the poorer grades to improve the quality. The manufacturer has learned by experience to make use of the different germs of the tobacco. But the chemist should not stop here. He should find out what the products of the growth of these germs are. This is possible because the germs can be isolated, cultivated, and the product of each individual germ determined, and eventually its identification or synthetic preparation.

Again, in Denmark, the practical manufacture of butter and cheese has been greatly advanced by the use of butter ferments, as they have been called. The flavor and aroma of butter and cheese are due to the products of a particular bacterium, or of several. Now these can and have been isolated, and to produce the best butter and cheese only those bacteria are used upon sterilized milk which give a desirable flavor, while normally those with undesirable products would also be present and interfere with the character of the butter and cheese. Here again the products of the growth of these bacteria should be studied, which in many instances would no doubt be found to be substances of easy synthetic preparation. It would be very much better to be able to add to a butter or cheese some particular extract which will impart the special flavor, rather than to have to inoculate the cheese and milk with a particular bacterium or mixture of bacteria for a desired quality. As has been well stated, we may see the time when each dairy is provided with a bacteria farm, and each particular brand of butter and cheese will have its corresponding originator, labeled and reared with as much care as is given to the cow from which the milk is obtained.

In their relation to the soil and plant life the germs and their

products are invaluable. Warrington and Winogradsky, in their isolation of the nitrifying organisms which convert nitrogenous matter into nitrites and nitrates, have thrown great light on the absorption of nitrogen by plants. Recently Winogradsky has described an organism which converts the nitrogen of the air directly into nitrates. Again, there are a number of germs that are ordinarily found in water or the soil which will reduce nitrates to nitrites or ammonia, as well as some pathogenic germs usually present in the soil which will flourish in artificial media in an atmosphere of nitrogen. We know that a subsoil, freshly turned, will not be productive until it has been exposed for some length of time to the air and moisture and to the action of the germs of the air. The plant does not take up directly in the form in which it exists in the soils, the mineral matter that it needs for its growth, but only when that is modified to a simpler form can it be utilized. Phosphorus is one of the elements which, whether combined in albuminoids or mineral salts, seems to be necessary for the growth of the germ, and is also necessary for the life of plants. By closely following the gradual changes in the artificial cultures of germs, we can arrive at a more definite understanding of the assimilation of mineral matter by the plant, as well as the fixation of carbon, the formation of starch and sugar, and possibly also, as has been suggested, of the building up of alkaloids.

I have only mentioned a few of the many directions in which a conjoint study of bacteria and their products are important with the desire of emphasizing the interest attaching to such investigations. It is along this line of research that the solution of many of the problems of life that have been a puzzle to both physiologist and chemist undoubtedly lies.

DETERMINATION OF THE CRYSTALLIZABLE SUGAR IN THE BEET.¹

BY H. PELLET.

TRANSLATED AND ABSTRACTED BY G. L. SPENCER, WASHINGTON, D. C.

THIS is an extensive article including a résumé of practically all that has been written by the leading authorities upon

¹ Read before the World's Congress of Chemists, August 22, 1893.

the subject, in addition to original methods by the author. The paper is divided into five parts.

The first part contains a brief outline of the methods employed for the determination of sugar since the beginning of the industry, or in fact since the work of Margraff on the beet in 1747, and includes the literature of 1886.

In the second part is included a review of the principal prizes which have been awarded for researches on the estimation of sugar in the beet.

In the third part is given a résumé of the different methods which may be applied for the direct determination of the sugar, and the principal details of the new cold and warm aqueous methods, as applied in the manufacture of sugar and the analysis of mother beets.

In the fourth part is given an examination of the matters existing in the beet which influence the determination of the sugar, notably raffinose, pectic substances and asparagine.

Finally, in the fifth part, note is made of the purchase and sale of beets according to their quality, and an examination of the various methods employed for this purpose is included.

This abstract relates simply to that portion of the third part of the paper which includes methods original with the author.

PROCESSES WHICH MAY BE APPLIED TO THE ANALYSIS OF THE
BEET FOR THE DIRECT DETERMINATION OF THE CRYSTALLIZABLE SUGAR WHICH IT CONTAINS.

The different methods may be divided into two classes, namely, chemical and physical (polariscopic). As the polariscopic methods are those usually employed we will omit a description of the chemical. The polariscopic methods may be divided into two groups; those employing alcohol as a solvent for extracting the sugar and those employing water. The process employing water, with which we shall specially deal, is that devised by the author and known as the method of instantaneous aqueous diffusion in the cold. In the instantaneous method, it is essential to obtain the beet pulp in an extremely fine state of division. Ordinary rasps cannot be employed for this purpose. For the analysis by this method the following rasps are recommended: First, for the analysis of entire beets, the conical rasps of Pellet

products are invaluable. Warring second, for the analysis of frag-
isolation of the nitrifying organic matters for the diffusion process.
matter into nitrites and nitrates. Leipzig; third, for the analysis of
absorption of nitrogen by plants. Second selection, the apparatus of
described an organism which is the *foret-râpe*. The rasp used in
directly into nitrates. Again the Hanriot is applicable.

are ordinarily found in water. In the process the pulp must be in a very
nitrates to nitrites or ammonium. It is forming a cream, but the parti-
usually present in the soil. A suitable amount of the pulp,
in an atmosphere of nitrogen. It is to protect it, is weighed into a
turned, will not be produced. If the normal weight for the Ger-
length of time to the air. If it is used the volume should be
germs of the air. The volume of pulp be taken the volume
form in which it exists. It is passed into the special flask with
needs for its growth, but water, then five to seven cc. of sub-
form can it be utilized. It is added and a little ether to reduce the
which, whether combined or not, is agitated with a rapid circular motion at
to be necessary for the process. The volume is now completed to 200 or 201.35 cc.
for the life of plants. The contents of the flask thoroughly

in the artificial culture. It is to be used after having acidulated the liquid
nite understanding of the process. It is glacial acetic acid. A 400 mm. tube is
plant, as well as the process. It gives the reading directly, corrected
and sugar, and possible. It is the volume of the solution. The diffusion is
building up of alkaline. It is complete, permitting the filtration to be made

I have only mentioned. It has been filled to the graduation and the con-
a conjoint study of the process. It is never necessary to heat the solu-
with the desire of the process. It is complete diffusion, unless the water should
investigations. It is approximating 0° C. For all ordinary labora-
of many of the processes. The water will be sufficiently warm.

physiologist and chemist. It is a large number of analyses per day, by this

It is a rack having six, twelve, or twenty-four holes,

It is also a continuous polariscope tube which

later on. Twelve to twenty flasks should be

of the polariscope.

TRANSLATED

THIS is an attempt to determine the different possible sources of error in the estimation
all that is to be considered. In the aqueous process there is,
the beet, those belonging only to the aqueous
here considered. In the aqueous process there is,
the possibility of the digestion or diffusion being incom-

¹ Read before the

plete, but this is very rare, since, owing to the simplicity of the operation, the flasks will always stand a sufficient time to obtain complete diffusion. In using the apparatus in the cold there is no danger at all of error, since a preliminary trial should be made to ascertain whether the pulp is sufficiently fine, and whether the water is of the proper temperature. There is a possibility of the solution of pectic substances which rotate the plane of polarization to the right. This error can only result from an insufficient amount of sub-acetate of lead. This inconvenience is easily avoided. The presence of pectic bodies may be shown in the following manner: Extract the pulp with cold water in large excess or with alcohol; treat the residue with boiling water and concentrate the liquid. This liquid will give a decided right-handed polarization amounting to more than 6.87 per cent. sugar on the weight of the beet. The same liquid, treated by sub-acetate of lead in sufficient quantity, will always polarize zero. Our work in this case is confirmed by Messrs. Chevron, Droixhe, and Weisberg.

Alcohol acts as sub-acetate of lead upon pectic matters and precipitates them entirely. It is for this reason that in the alcoholic solution two or three drops of sub-acetate of lead are sufficient for clarification, and for the complete precipitation of the pectic matters. It is hence easy to see how different results may be obtained in using the alcoholic or the water method upon the same pulp. Such differences might amount to from two to three per cent. of sugar calculated on the weight of the beet. As we have become better acquainted with the sources of error, the experiments have been repeated, and the adversaries of the aqueous method have all recognized that there are no plus polarizing substances in the beet not precipitable by lead and which are only thrown down completely, as they have stated, by alcohol.

In 1886 and 1887 many chemists published articles in which they attempted to demonstrate that alcohol, in fact, furnished results lower than those obtained by the water method, and which they then attributed to some particular substances precipitable by alcohol, and not by the sub-acetate of lead. But all have acknowledged later on that there were evidently diverse causes of error in their experiments, and have published statements

OF

papers, and have shown
and aqueous methods.
valuable, since at first
attacked by critics who
There is still another possi-
in the cold. This is
to the pulp, and may
to ether being replaced
to other faulty manipu-
easily obviated. Numer-
demonstrated that the aqueous
gives practically the same
the alcoholic or the hot water

ANEQUEOUS AQUEOUS DIFFUSION THE EXAMINATION SEETS.

removed from the beet by the
and analyzed as described. This
and the usual manipulation. A
will be described more in detail,
method of working, that is with-
per day have been made in the
and in the sugar house of Vaux

others without the use of a balance,
room is employed. This sound is
of a lever, a knife is made to
a portion of it. A proper arrange-
the beet at a proper angle to the
with parallel blades which are
remove a cylindrical portion of the
under the control of the operator.
cut a cylinder of a certain size, which
of the operator, it may be used
and will cut a cylinder of practically the
The weights of the following cylinders
an idea of the accuracy of this method:

| No. | Weight,
grams. |
|---------|-------------------|
| 1..... | 6.245 |
| 2..... | 6.265 |
| 3..... | 6.290 |
| 4..... | 6.370 |
| 5..... | 6.245 |
| 6..... | 6.285 |
| 7..... | 6.365 |
| 8..... | 6.250 |
| 9..... | 6.335 |
| 10..... | 6.240 |
| 11..... | 6.330 |
| 12..... | 6.390 |
| 13..... | 6.370 |
| 14..... | 6.270 |
| 15..... | 6.310 |
| 16..... | 6.300 |

Average, 6.304 grams.

If one will consider a beet of average richness as containing fifteen per cent. sucrose the minimum weight given in the above list would show 14.85 sugar and the maximum 15.2, an extreme difference of 0.35 or 0.15 to 0.20 above and below the mean. These figures approximate the required weight with sufficient accuracy for actual practice and for use with the special apparatus devised by Hanriot, we have found it a very valuable adjunct. Hanriot's apparatus is so arranged that the sample of beet, of the required weight, when placed in a proper receptacle is transferred to a mill where it is ground to a fine pulp. Immediately after grinding, by a suitable manipulation of a valve and rubber bulb containing water, the fine pulp is washed into the sugar flask and is ready for analysis. The Hanriot apparatus is then quickly washed, by means of a special valve arrangement, and is ready for another sample. Preliminary to commencing the analytical work, the sound is adjusted to give the most convenient weight of pulp, for the polariscope in use. This may be 6 grams, 5.12 grams, or 4.05 grams, according to the requirements of the instrument. But little adjustment is necessary to so set the knives that they will cut a cylinder of the proper diameter and length to give the required weight. In this class of analysis, it is unnecessary to take account of the influence of the volume of the marc of the beet.

reviewing those made in their first papers, and have shown perfect concordance between the alcoholic and aqueous methods, when properly carried out. This is quite valuable, since at first the aqueous methods were vigorously attacked by critics who now acknowledge their reliability. There is still another possible source of error in the aqueous method in the cold. This is caused by air bubbles remaining attached to the pulp, and may be due to an insufficient use of ether, to ether being replaced by alcohol, to insufficient agitation, or to other faulty manipulations. This error, it may be seen, is easily obviated. Numerous parallel experiments have demonstrated that the aqueous instantaneous method in the cold, gives practically the same results as those obtained by either the alcoholic or the hot water methods.

APPLICATION OF THE INSTANTANEOUS AQUEOUS DIFFUSION
PROCESS IN THE COLD TO THE EXAMINATION
OF MOTHER BEETS.

A portion of the pulp may be removed from the beet by the *foret-râpe* of Keil and Dolle and analyzed as described. This requires simply a weighing and the usual manipulation. A simpler method, and one which will be described more in detail, obviates all weighings. In this method of working, that is without weighing, 8,300 analyses per day have been made in the establishment of Mr. Legras, and in the sugar house of Vaux sous Laon.

In the analysis of beet mothers without the use of a balance, the sound invented by Lindeboom is employed. This sound is so arranged that by the movement of a lever, a knife is made to penetrate the beet and remove a portion of it. A proper arrangement is provided for inclining the beet at a proper angle to the knife. The knife is arranged with parallel blades which are adjustable, and which will remove a cylindrical portion of the beet of a size which is perfectly under the control of the operator. After adjusting the knife to cut a cylinder of a certain size, which is determined by the convenience of the operator, it may be used for a number of samples and will cut a cylinder of practically the same weight at all times. The weights of the following cylinders cut in this way will give an idea of the accuracy of this method =

| No. | Weight,
grams. |
|---------|-------------------|
| 1..... | 6.245 |
| 2..... | 6.265 |
| 3..... | 6.290 |
| 4..... | 6.370 |
| 5..... | 6.245 |
| 6..... | 6.285 |
| 7..... | 6.365 |
| 8..... | 6.250 |
| 9..... | 6.335 |
| 10..... | 6.240 |
| 11..... | 6.330 |
| 12..... | 6.390 |
| 13..... | 6.370 |
| 14..... | 6.270 |
| 15..... | 6.310 |
| 16..... | 6.300 |

Average, 6.304 grams.

One will consider a beet of average richness as containing 14.85 per cent. sucrose the minimum weight given in the above would show 14.85 sugar and the maximum 15.2, an extreme difference of 0.35 or 0.15 to 0.20 above and below the mean. These figures approximate the required weight with sufficient accuracy for actual practice and for use with the special apparatus devised by Hanriot, we have found it a very valuable method. Hanriot's apparatus is so arranged that the sample of beet of the required weight, when placed in a proper receptacle is transferred to a mill where it is ground to a fine pulp. Immediately after grinding, by a suitable manipulation of a glass and rubber bulb containing water, the fine pulp is washed into the sugar flask and is ready for analysis. The Hanriot apparatus is then quickly washed, by means of a special valve arrangement, and is ready for another sample. Preliminary to commencing the analytical work, the sound is adjusted to give the most convenient weight of pulp, for the polariscope in use. This may be 6 grams, 5.12 grams, or 4.05 grams, according to the requirements of the instrument. But little adjustment is necessary to so set the knives that they will cut a cylinder of proper diameter and length to give the required weight. In this class of analysis, it is unnecessary to take account of the influence of the volume of the marc of the beet.

In the analysis of seed beets, Mr. Hanriot has suggested the use of electric signals for assorting the roots. Electric contacts are arranged on the scale of the instrument so that when this is turned to a certain point, corresponding to a certain richness of the beet, a signal will be sounded on a bell, and when turned to a certain other point a signal will be sounded on a bell of different tone, indicating in general the richness of the sample and showing the workmen how to distribute the roots.

CONTINUOUS TUBE FOR THE POLARIZATION
OF ALL SOLUTIONS.

In many cases the manufacturer of sugar, the refiner or the seed producer, is obliged to make a very large number of analyses of the same class and as rapidly as possible. The work required in seed selection is an example. In this industry it is often necessary to make 3,000, 4,000, 5,000, and even 8,000 or more analyses of mother beets in a day.

With ordinary apparatus it is admitted that with one polariscope a single observer may make from 500 to 600 or even 1,000 analyses in a day, provided one has a sufficient number of observation tubes, that is, from twenty to fifty. The continuous tube permits this work with much less labor, far greater rapidity and requires but one observation tube. This instrument was devised especially for use in the analysis of mother beets.

Many difficulties were overcome before this tube was constructed in a satisfactory form. As now used there is a small tube at each extremity, one of which is termed the funnel and connects directly and exactly at the extremity of the observation tube against the glass; the other is a similar tube but is placed at a slight angle with the observation tube. This small tube connects with the sink and is used to get rid of the solutions after they have been polarized. This arrangement of the observation tube permits the displacement of one solution by another. In practice, the observation tube is never removed from the polariscope. At the start it is filled with water, slightly acidulated with acetic acid, care being taken to remove all air bubbles. The solution to be observed is now passed in at the funnel tube displacing the water, driving it out through the tube at the opposite end. When another solution is ready for examination, it is

simply necessary to pour it into the funnel and, as before, displace the preceding solution. The chemist at the polariscope will at first observe striae, which diminish rapidly, and finally the solution will become perfectly clear. As soon as the liquid becomes clear the observation may be made. While the chemist is entering the reading in his note book, an assistant introduces a new solution at the funnel, and the instrument is ready for another observation. In this way an observer can easily make four readings in a minute, but even if he could make but two, he would attain a speed twice as great as is possible with the ordinary polariscopic methods and with far less labor. In the analysis of beet mothers, where a slight difference is of no importance, an observer can easily make from six to ten readings per minute.

A special disposition of the apparatus may be made which permits filling the tube by siphonage. In this way from eight to twelve solutions per minute may be polarized.

EXPERT TESTIMONY.

BY WM. P. MASON.

A NUMBER of years ago several very able articles appeared in *Nature*, upon the subject of Expert Testimony, showing how desirable it is to have the scientific witness removed as far as possible from the position of a partisan, and suggesting that such an end could be best obtained by having the experts employed by the bench rather than by the bar. Some recent experiences of my own, which I beg permission to recount, call to my mind those "Nature" articles very forcibly. A poison case in which I was lately employed, may be roughly outlined as follows:

Much arsenic and a very little zinc were found in the stomach.

The body had not been embalmed, but cloths wrung out in an embalming fluid containing zinc and arsenic had been spread upon the face and chest.

Medical testimony showed that no fluid could have run down

¹ Read at the Baltimore meeting, December 28, 1893.

the throat. Knowing the relative proportions of zinc and arsenic in the embalming fluid, the quantity of arsenic found in the stomach was twelve times larger than it should have been to have balanced the zinc also there present, assuming them to have both come from the introduction of the said embalming fluid by cadaveric imbibition. Other circumstantial evidence was greatly against the prisoner.

At the time of my appearing for the people, on the occasion of the first trial of the case, my direct testimony brought out very strongly the fact of a fatal quantity of arsenic having been found in the stomach, but no opportunity was given me to testify to the presence of the zinc found there as well, although the fact of its existence in the body was known to the prosecution through my preliminary report. Through ignorance of the nature of such report on the part of the defence, no change was made in the character of my testimony during the cross-examination, and I was permitted to leave the witness-stand with a portion of my story untold. No witnesses were called for the defence, and the case was given to the jury with the darkest of prospects for the prisoner.

For many reasons, unnecessary to recount here, I was distinctly of the opinion that murder had been committed, but I felt nevertheless that common justice demanded that the prisoner should have been entitled to whatever doubt could have been thrown upon the minds of the jury, no matter how far-fetched the foundations for such doubt might have been.

The first trial having resulted in a disagreement of the jury I was pleased to learn, before the second hearing of the case began, that the defence was prepared to go into the question of the embalming fluid, for the responsibility of permitting only a part of what I knew to be drawn from me, to the entire exclusion of the remaining portion, was greater than I wished to assume. The nature of my report to the coroner having been established, and certain opinions relating thereto having been fully ventilated, the jury were possessed of "reasonable doubt" and acquitted the prisoner. What now were the duties of the expert upon the occasion of the first trial of this case and how should he have constructed the meaning of his oath.

One eminent legal light, to whom the question was referred, held that the expert was distinctly the property of the side employing him, and that his duty was simply to answer truthfully the questions put to him, without attempting to enlighten the court upon facts known to him, but not brought out by the examination, no matter how vital such facts might be.

Another held that although the above course would be proper in a civil case, yet in a matter involving life and death the witness should insist upon the court becoming acquainted with his whole story. Do not such differences in legal opinion make it yet more desirable that the expert, at least in capital cases, should be the employee of the bench, rather than of the bar, in order that whatever investigations are made may be entirely open to public knowledge and criticism?

DISCUSSION.—Dr. Wiley: I hope that at some time in the future we shall be able to discuss this subject more fully. It is one which vitally interests most of us.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 2.]

A NEW METHOD OF ANALYZING FATS AND RESINS.

BY PARKER C. McILHINEY, PH.B., A. M.

Received January 5, 1894.

A number of processes have been proposed and used for the analysis of fats depending upon the power possessed by their unsaturated constituents to absorb by direct addition two or four atoms of bromine or iodine.

Allen, *Analyst*, **6**, 177, proposed the use of an aqueous solution of sodium hypobromite to be added to a weighed quantity of the oil together with sufficient hydrochloric acid to liberate the bromine which then acts upon the oil. An excess having been added its amount is determined with sodium thiosulphate after adding potassium iodide.

Mills and Snodgrass, *J. Soc. Chem. Ind.*, **2**, 436, added a solution of bromine in carbon disulphide to a solution of the fat in the same solvent until an excess has been added as indicated by the red color of the bromine remaining permanent for fifteen

minutes, and then a solution of potassium iodide and determined the excess with thiosulphate.

Mills and Akitt, *J. Soc. Chem. Ind.*, **3**, 65, proposed to substitute carbon tetrachloride for carbon disulphide and to determine the excess by a solution of β naphthol in the same solvent.

Hübl, *Dingler's Poly. J.*, **253**, 281, and *J. Soc. Chem. Ind.*, **3**, 641, suggested the use of a solution containing twenty-five grams of iodine and thirty grams of mercuric chloride dissolved in one liter of alcohol, a known measure of the reagent to be added to a weighed portion of the oil and allowed to remain tightly stoppered for a certain length of time when the excess is determined with thiosulphate.

Levallois, *J. pharm. chim.*, 1887, **1**, 334, used bromine water, adding it, in just sufficient excess to slightly color the liquid, to the fatty acids obtained from the oil suspended in water.

Halphen, *J. pharm. chim.*, 1889, **20**, 247, used bromine water in excess determining the amount of excess with sodium hydroxide.

Gantter, *Ztschr. anal. chem.*, 1893, 178, suggested the use as a reagent of iodine dissolved in carbon tetrachloride.

The aim of all these processes is to determine the amount of halogen which the substance under examination will absorb by addition, but the figures obtained represent this only approximately even when substances which easily form substitution products are absent. Some substitution takes place with almost all oils, and with rosin oil, rosin, and probably most other resins, substitution causes the entire absorption.

The extent to which this substitution takes place depends upon the nature of the substance operated upon, and varies with different oils and resins, and a determination of the amount of halogen so absorbed may serve as a means of identifying and in some cases determining them.

The following process has been devised for determining the amount of bromine which oils and resins can absorb by addition, (which will be called the "Bromine Addition Figure"), and at the same time the amount of bromine which replaces hydrogen the action being allowed to continue eighteen hours in the dark; this gives the "Bromine Substitution Figure." The first figure

gives in most cases the same information as the Hübl figure but is more reliable, while the second figure is a measure of the activity of the saturated constituents toward bromine.

It depends upon the fact that bromine in forming substitution compounds forms a molecule of hydrobromic acid for every atom of bromine which replaces hydrogen, while in forming additive compounds no hydrobromic acid is formed.

It was found impossible to use iodine alone as the addition figures are then very much too low and there is little difference between the substitution figures of bodies of unlike character.

The following solutions are used:

| | |
|--------------------------------------|----------------|
| Bromine in carbon tetrachloride..... | $\frac{N}{8}$ |
| Sodium thiosulphate..... | $\frac{N}{10}$ |
| Potassium hydroxide..... | $\frac{N}{10}$ |

0.250–1.000 gram of the substance is dissolved in ten cc. of carbon tetrachloride in a bottle of 500 cc. capacity provided with a carefully ground glass stopper. An excess of bromine solution is added, the bottle tightly stoppered and placed in a dark closet. No water or alcohol should be present and light should be excluded as far as practicable. At the end of eighteen hours the bottle is cooled with ice to form a partial vacuum, and a piece of wide rubber tubing about one and one-half inches long is slipped over the lip of the bottle so as to form a well about the stopper. This well is filled with water and the stopper carefully lifted when the water will be sucked into the bottle and dissolve the hydrobromic acid present. When about twenty-five cc. of water have been added in this way, the bottle is well shaken and 10–20 cc. of twenty per cent. potassium iodide solution added. The excess of bromine acts on the potassium iodide, liberating a corresponding amount of iodine which is titrated with $\frac{N}{10}$ thiosulphate after adding about seventy-five cc. more water, using starch as an indicator. The total bromine absorption is calculated from the difference between the amount of thiosulphate required for the bromine solution added and the amount required for the excess. The contents of the bottle are now transferred to a separatory funnel and the aqueous portion separated, filtered through a cloth filter, a few drops of thiosulphate added if the solution is blue, and this is then titrated with $\frac{N}{10}$ potassium

hydroxide using methyl orange as indicator. The end reaction is best observed by using a porcelain casserole to contain the solution, adding the alkali in slight excess and titrating back with $\frac{N}{10}$ hydrochloric acid until the pink acid tint just reappears. From the number of cubic centimeters of alkali used the amount of bromine present as hydrobromic acid is calculated, and when expressed in per cent. gives the bromine substitution figure because for every atom of bromine which has replaced an atom of hydrogen, one molecule of hydrobromic acid has been formed. Twice the bromine substitution figure subtracted from the total absorption gives the bromine addition figure.

The following results were obtained:

| Substance. | Total bromine
absorption,
eighteen hours. | Bromine,
addition
figure. | Bromine,
substitution
figure. |
|-------------------------------|---|---------------------------------|-------------------------------------|
| W. G. Rosin..... | 212.7 | 0.0 | 106.35 |
| E. Rosin..... | 206.5 | 0.0 | 103.25 |
| Second run Rosin Oil (a).... | 116.2 | 0.0 | 58.1 |
| “ “ “ “ (b).... | 114.7 | 0.0 | 57.35 |
| American Raw Linseed Oil ... | 102.88 | 102.88 | 0.0 |
| Same Oil Boiled..... | 103.92 | 103.92 | 0.0 |
| White Salad Cotton-seed Oil.. | 65.54 | 64.26 | 0.64 |
| Sperm Oil | 56.60 | 54.52 | 1.04 |

A consideration of the above figures shows that the results are much more instructive than those obtained by the Hübl process which is the one in common use. Rosin oil, rosin, and other resins may be detected and determined in mixture with fatty oils, or, if they are present in known quantity, the character of the fatty oil may be determined. Investigations which are being made on a large number of oils and resins will probably furnish analytical data for the analysis of oils and varnishes.

ON THE DETERMINATION OF PHOSPHORIC ACID.¹

By H. PEMBERTON, JR.

LAST autumn I described a process for determining phosphoric acid by titration of the ammonium phosphomolybdate with standard alkali. (This JOURNAL, 15, 382.) The ratio

¹ Read at the stated meeting of the Chemical Section of the Franklin Institute, held February 20, 1894.

between the P_2O_5 of the precipitate and the standard alkali was determined and found to be 23.2 molecules of Na_2O to one molecule of P_2O_5 . Upon this ratio, as determined by direct analysis, the standard solution was prepared of such strength that one cubic centimeter should be equal to one milligram of P_2O_5 by diluting 326.5 cubic centimeters of normal alkali to one liter. The analyses upon which this ratio (23.2 molecules) was determined were carefully made. I was, therefore, at a loss to know the cause of the variation of this figure from the theoretical ratio of exactly twenty-three molecules of Na_2O . The difference is of more importance than might at first thought, be supposed, since the strength of the alkali solution is based upon the figure determined empirically, and not upon the theoretical one. If the 23.2 proportion is wrong and twenty-three correct, a standard solution based upon the former ratio would give too low results in the proportion of 23.2 : 23.0. Thus a phosphate rock containing eighty per cent. calcium phosphate would appear, by such an analysis, to contain only 79.31 per cent.

It was decided, therefore, to repeat this part of the work, and in this re-examination the conditions were the same as those previously existing, except in one particular: the amount of phosphoric acid operated upon was smaller than that previously used. By referring to the original paper, it will be found that about eighty cubic centimeters of alkali were used in each of the titrations in question. This represents a quantity of the yellow precipitate much larger than would ever be obtained in the analysis of even the richest phosphate rocks; and in operating upon so large a precipitate the liability of error from incomplete washing is great. Any free acid remaining in the precipitate would, of course, result in too high a reading of the burette, with a corresponding error in the standardizing of the solution.

The following are the results obtained in this re-examination:

Some di-sodium hydrogen phosphate, bought as chemically pure, was dissolved in hot distilled water, filtered, and crystallized; the crystals were washed, dissolved again in water, and recrystallized. Of the resulting crop of crystals, about forty-five grams were dissolved in one-half liter of water. The strength of this solution was then determined.

| | Weight of
Na_2HPO_4
solution,
grams. | Grams. |
|----------|---|---|
| I..... | 20.0814 | gave 0.7581 $\text{Na}_4\text{P}_2\text{O}_7$ |
| II..... | 17.9585 | gave 0.6778 $\text{Na}_4\text{P}_2\text{O}_7$ |
| III..... | 36.9115 | gave 1.1652 $\text{Mg}_2\text{P}_2\text{O}_7$ |

The magnesium-ammonium phosphate precipitate was filtered, dissolved in acid and reprecipitated by ammonia.

By a coincidence each of these three determinations gave precisely the same result; *viz.*,

TABLE I.

| | Grams
P_2O_5 in
10 grams of
solution. |
|----------|--|
| I..... | = 0.2014 |
| II..... | = 0.2014 |
| III..... | = 0.2014 |

Therefore, ten grams of the sodium phosphate solution contained 0.2014 grams P_2O_5 .

Weighed portions of this same solution were now precipitated by ammonium molybdate, thoroughly washed and titrated. The results are given in Table II.

TABLE II.

| I. | II.
Grams
Na_2HPO_4
solution
taken. | III.
Equiva-
lent to
grams
P_2O_5 . | IV.
cc. of
KHO
solution
used. |
|--------|---|---|---|
| A..... | 2.0410 | 0.04110 | 41.05 |
| B..... | 2.3710 | 0.04775 | 47.70 |
| C..... | 2.2920 | 0.04616 | 46.20 |
| D..... | 2.4690 | 0.04972 | 49.60 |

Dividing the figures in Column III by those in Column IV, and multiplying the result by 100, we obtain the number of milligrams corresponding to 100 cubic centimeters of the potassium hydroxide solution, as follows:

TABLE III.

| | Mgms. P_2O_5 . |
|--------------|--------------------------------|
| A..... | = 100.12 |
| B..... | = 100.11 |
| C..... | = 99.91 |
| D..... | = 100.24 |
| Average..... | = 100.09 |

Therefore, 100 cubic centimeters of the potassium hydroxide

solution neutralize an amount of the yellow precipitate corresponding to 100.09 milligrams of P_2O_5 .

The standard acid was now titrated against the standard alkali, using phenolphthalein as the indicator, whereby the two solutions were found to be of exactly equal strength.

The standard acid was then titrated against pure sodium carbonate, using phenolphthalein at boiling heat:

| | Grams Na_2CO_3
used. | cc. of acid
used. | 100 cc. acid equal to
mgms. Na_2CO_3 . |
|---------|---------------------------|----------------------|---|
| I..... | 0.9099 | 52.95 | 1719 |
| II..... | 0.9168 | 53.35 | 1719 |

Therefore, 100 cubic centimeters of acid are equivalent to 1719 milligrams sodium carbonate, and since the alkali solution is of the same strength as the acid, 100 cubic centimeters of it also are equivalent to 1719 milligrams sodium carbonate.

As we have already seen, by Table III, that 100 cubic centimeters of the alkali are required to neutralize 100.09 milligrams of P_2O_5 (in the form of ammonium phosphomolybdate), it follows that 1719 milligrams sodium carbonate are required for 100.09 milligrams P_2O_5 .

Dividing each by its molecular weight we have

$$\begin{aligned} \text{for } P_2O_5, \frac{100.09}{142.06} &= 0.7045 \\ \text{for } Na_2CO_3, \frac{1719.0}{106.1} &= 16.20 \end{aligned}$$

Therefore,

$$P_2O_5 : Na_2CO_3 = 0.7045 : 16.20 = 1 : 22.99$$

In other words, 23 molecules of sodium carbonate (or of Na_2O) are required to neutralize the yellow precipitate containing one molecule of P_2O_5 , and the former figure (that given in my paper of last autumn) 23.2 molecules, is incorrect.

Referring to Table II of the present paper, it may be stated that in analysis A the yellow precipitate was washed on an ordinary filter without using suction, the precipitate being washed on the filter, transferred to the beaker and then again filtered and washed. In analysis B, of the same table, the precipitate was washed on the ordinary filter, with the aid of the suction pump. In analyses C and D, the precipitates were washed with suction on a porcelain funnel with a fixed perforated plate in it.

This form of funnel is known as the Hirsch funnel.¹

As in all cases the results were nearly identical; it is evident that the different methods of washing the precipitate had no influence upon the result. Exactly twenty-three molecules of Na_2O are required for one molecule of P_2O_5 . The standard acid is prepared by diluting 323.7 cubic centimeters of normal sulphuric acid to one liter, and not 326.5 cubic centimeters as previously stated. The alkali solution, after removing carbon dioxide by barium hydroxide, is brought to the same strength as the acid, volume for volume.

One cubic centimeter of either solution is then equal to one milligram of P_2O_5 .

PHILADELPHIA, PA., February 20, 1894.

NOTE ON PEMBERTON'S METHOD OF PHOSPHORIC ACID DETERMINATION AS COMPARED WITH THE OFFICIAL METHODS.²

BY WM. C. DAY AND A. P. BRYANT.

HAVING occasion to make a series of determinations of phosphoric acid in Florida phosphate rock, we have used the method recently described by Mr. H. Pemberton, Jr., and incidentally have made a number of comparisons between it and the official method. The following are the results:

GRAVIMETRIC DETERMINATIONS.

No. 1. From 0.7867 gram $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$, obtained 0.2426 gram $\text{Mg}_2\text{P}_2\text{O}_7$

No. 1. From 1.1100 grams $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$, obtained 0.3433 gram $\text{Mg}_2\text{P}_2\text{O}_7$

No. 2. From 1.0000 gram Florida rock, obtained 0.5828 gram $\text{Mg}_2\text{P}_2\text{O}_7$

No. 3. From 0.3807 gram Florida rock, obtained 0.0262 gram $\text{Mg}_2\text{P}_2\text{O}_7$

No. 3. From 0.4831 gram Florida rock, obtained 0.0333 gram $\text{Mg}_2\text{P}_2\text{O}_7$

No. 4. From 1.0036 grams Florida rock, obtained 0.0227 gram $\text{Mg}_2\text{P}_2\text{O}_7$

¹ To be had from Bullock and Crenshaw, Philadelphia. A disk of filter paper of the diameter of an American silver quarter dollar (fifteen-sixteenths inch) is used, when employing the smallest size funnel. I can highly recommend this funnel in all cases in which the precipitate is to be titrated. The precipitate presents a perfectly flat surface, is easily and quickly washed, and is readily transferred with the aid of the wash bottle to the beaker. The funnel can be employed only when using the suction pump, but it has the advantage of not requiring a platinum cone, and the size of the filter is reduced to a minimum.

² Read at the stated meeting of the Chemical Section, of the Franklin Institute held February 20, 1894.

DETERMINATIONS BY PEMBERTON'S METHOD.

No. 1 used 1.0737 grams $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$ and 22.88 cubic centimeters KOH solution and 1.85 cubic centimeters acid.

No. 1 used 1.0370 grams $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$ and 21.30 cubic centimeters KOH solution and 0.80 cubic centimeter acid.

No. 2 used 1.0000 gram Florida rock and 41.85 cubic centimeters KOH and 5.05 cubic centimeters acid.

No. 3 used 1.0000 gram Florida rock and 7.55 cubic centimeters KOH and 3.10 cubic centimeters acid.

No. 4 used 1.0000 Florida rock and 6.75 cubic centimeters KOH and 5.50 cubic centimeters acid.

Strength of H_2SO_4 used 1 cubic centimeter = 0.015998 gram H_2SO_4 .

Strength of potassium hydroxide solution 1 cubic centimeter = 0.01847 KOH.

The percentages of P_2O_5 , calculated from the foregoing determinations, are :

| Substance. | Gravimetric. Pemberton. | |
|---------------------------------------|-------------------------|-------|
| No. 1, sodium hydrogen phosphate..... | 19.72 | 19.73 |
| No. 1, sodium hydrogen phosphate..... | 19.78 | 19.99 |
| No. 2, Florida rock..... | 37.28 | 37.22 |
| No. 3, Florida rock..... | 4.40 | 4.53 |
| No. 3, Florida rock..... | 4.41 | ... |
| No. 4, Florida rock..... | 1.45 | 1.32 |

It is evident from the above figures that the agreement between the results of the two methods is as close as could be desired. Inasmuch as the Pemberton method is of extreme accuracy, is very easily carried out and effects a great saving of time and labor over the official method, it is well worthy of extended use. We have found that the author's statement of the time required for a single determination, namely, thirty to forty minutes from the time the solution is measured out for titration, is entirely reasonable. Omitting filtration of silica makes no difference in the accuracy of the results.

SWARTHMORE COLLEGE, PA., February 20, 1894.

THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(Continued from Page 273.)

BY THOMAS B. STILLMAN, PH.D.

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[TO BE CONTINUED.]

INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

SUB-COMMITTEE ON METHODS.¹

BULLETIN No. 2.

CIRCULAR TO IRON AND STEEL CHEMISTS ON METHOD OF DETERMINING PHOSPHORUS.

AT the World's Congress of Chemists in Chicago a Sub-Committee of the original Committee on International Standards for the Analysis of Iron and Steel was appointed to

¹ The Sub-Committee on Methods for the Analysis of Iron and Steel, have sent the following bulletin to the iron and steel chemists of the country, so far as they could get their names. They earnestly request that any who do not receive a copy of the circular, but who do see this, will comply with the request of the bulletin, the same as though they had received a circular direct.

consider the subject of Standard Methods.

This sub-committee consists of Dr. C. B. Dudley, Chairman, Messrs. A. A. Blair, W. P. Barba, P. W. Shimer, and T. M. Drown. It has recently held a meeting and has decided to recommend standard methods in iron and steel analysis to be used as the basis of commercial transactions. The sub-committee fully appreciates the fact that these methods, to have the highest value, should be in facility and in time of execution such that they will readily recommend themselves for daily use in iron and steel works.

To further this end the sub-committee wishes to have the co-operation of the iron and steel chemists of the country, and to ask them for a brief outline of the processes or methods they use and prefer for the determination of different elements in iron and steel, and for such other information and suggestions as they think will aid it in the work before it. The sub-committee recognizes the fact that it will add immensely to its efficiency and value if the iron and steel analysts of the country will take a personal interest in it, and aid it by their counsel and active influence.

You are therefore requested to send to the chairman of the sub-committee, as soon as convenient, such an outline as you may deem sufficient to fully describe your practice. It is suggested that you follow the general plan here indicated, by answering the following questions, which may be referred to by number to save you unnecessary trouble:

First. What general method do you use for the determination of phosphorus in iron and steel?

Second. What special precautions do you consider necessary to make this method reliable?

Third. What precautions do you take to prevent the interference of arsenic?

Fourth. What factors do you use in your calculations?

Fifth. What variations do you introduce in the case of iron ores or slags?

Sixth. Do you use the same method in pig iron and steel and do you consider the results equally reliable?

Seventh. Do you ever examine the residues insoluble in acid,

in pig irons, or iron ores, and do you ever find phosphorus in them?

Eighth. Are all your determinations made by the same method, or do you check your work by reference to another method, and if so, what method do you use for this purpose?

Ninth. How many determinations do you make a day in your laboratory under ordinary circumstances?

Tenth. What do you consider the greatest length of time necessary to obtain a result, permissible in your work?

The sub-committee begs that you will send at the earliest possible moment as full replies to all or any of the above questions as you conveniently can, and assures you that in making use of any details that may be original with you, you shall have full credit. You will likewise be furnished with copies of the various reports.

CHAS. B. DUDLEY,

Chairman Sub-Committee,

APPROVED,

J. W. LANGLEY,

ALTOONA, PA.

Chairman Com. on Int. Standards.

ERRATUM.

In the column showing percentages for the No. 2 steel on page 219 this number, 0.041 should read 0.048.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

ON THE DETERMINATION OF PHOSPHORIC ACID
AS MAGNESIUM PYROPHOSPHATE.¹

BY HUGO NEUBAUER.

TRANSLATED AND ABSTRACTED BY K. P. MCELROY.

AFTER giving a brief history of the molybdenum method for the determination of phosphoric acid, Herr Neubauer states his reasons for thinking this method undeserving of its high repute for accuracy. He next gives the results of a long investigation of the sources of error inherent in the method.

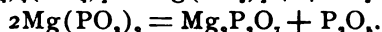
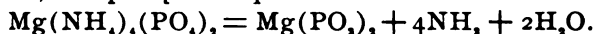
As a standard silver orthophosphate was employed, this salt being chosen partly because of its perfectly definite composition, partly because of the ease with which the base could be estimated. Magnesium ammonium phosphate was rejected for this purpose because it was not thought proper to have the same salt serve as both the beginning and the end. Disodium phosphate was rejected because, of its tendency to absorb carbonic acid. In the first series of experiments on the molybdate method (Wagner's modification), the amount of phosphoric acid found was a trifle less than that known to have been used, the discrepancy ranging from 0.3 mgm. on 84.2 mgms. P_2O_5 to 2.7 mgms. on 166.8 mgms. P_2O_5 . Two explanations could be made of this loss—either that the precipitations were not complete or that volatilization of the phosphoric acid occurred during the ignition of the magnesium salt previous to weighing. Neubauer rejected the former explanation in favor of the latter, adducing a series of

¹ Presented to the World's Chemical Congress, Chicago, August 22, 1893.

experiments in favor of his view. The lid of a platinum crucible was covered with a layer of magnesium hydroxide on the under side and ignited till magnesium oxide was formed and the weight of the lid remained constant. A filter containing magnesium phosphate was then burned in the crucible and after the combustion of the paper, the lid was placed in position and the salt ignited to constant weight. The lid was found to have increased in weight in amounts varying from 0.2 mgm. to 3.8 mgms. The smaller amount was found where the phosphoric acid was directly precipitated and also in a case where magnesium ammonium phosphate reputed to be chemically pure was directly ignited. The largest increase in weight was found in cases where large quantities (five grams) of ammonium chloride or molybdate were added previous to the precipitation of the double phosphate. In the precipitate obtained by the Wagner process (in this method the ammoniacal solution of the yellow precipitate is not neutralized previous to adding the magnesia mixture) the increase varied from 0.5 mgm. to 2.0 mgms. On solution of the magnesia layer on the lid, phosphoric acid was detected by the molybdate reaction. The observation is made that precipitates exposed to the heat of a common Bunsen burner are but little below the truth, while the weights of large precipitates obtained by the molybdate method are often several milligrams too low after strong ignition. The argument is made that the molybdic acid cannot be responsible for this peculiar behavior, since the precipitate when washed till the chlorine reaction disappears contains but an insignificant amount of this substance. Magnesium ammonium phosphate covered before ignition with a weighed amount of lime or magnesia, weighs more than a similar precipitate ignited without this addition, in case an excess of ammonium salts has been present during the precipitation. If the washed precipitate of magnesium ammonium phosphate is dissolved in a very little hydrochloric acid, ammonia in excess added and then two cc. of magnesia mixture, the double precipitated salt will weigh more than it would have done otherwise in case much ammonium molybdate was originally present.

From these facts the conclusion is drawn that in the presence of an excess of ammonium salts, the magnesian precipitate is not

pure dimagnesium ammonium phosphate (MgNH_4PO_4), but contains more or less monomagnesium ammonium phosphate ($\text{Mg}(\text{NH}_4)(\text{PO}_4)$). This latter salt decomposes on ignition into magnesium metaphosphate, ammonia, and water. On further ignition, this phosphate becomes converted into pyrophosphate, and phosphorus pentoxide is set free and volatilized.



The greater the concentration of the ammonium salts, the larger the amount of monomagnesium salt which will be formed. For this reason the prevailing ideas relative to the concentration of the solutions to be precipitated are erroneous and more accurate results can be obtained by greater dilution.

Two chances of error exist in the determination of phosphoric acid by the magnesian method—first, that the precipitate may contain too much magnesia, second, that it may contain too little. The second error is readily detected by the method already given. The other may be detected by Tollen's method (*J. Landw.*, 1882, 30, 48), which consists in suspending the ignited phosphate in water, adding a little dilute solution of silver nitrate and heating. In the presence of an excess of magnesium, silver orthophosphate is formed and recognized by its yellow color. The reaction is sufficiently sensitive.

Experiments were made with solution of pure magnesium ammonium phosphate containing various amounts of ammonium chloride. In one solution containing 300 mgms. of the chloride, half a milligram of magnesia was found in the filtrate after precipitation by ammonia, and the same quantity of phosphorus pentoxide was volatilized on ignition of the precipitate. In another case where 2.5 grams of ammonium chloride were present, the loss in magnesia and phosphoric oxide were respectively 1.1 and 1.6 mgms. In a third where five grams were employed, the losses were 3.2 and 4.4 mgms. respectively. Finally, phosphoric acid (44.8 mgms.) was precipitated in the presence of 200 cc. of approximately saturated solution of ammonium chloride. The losses reached the large figures of 12.7 and 15.6 mgms. respectively for MgO and P_2O_5 . The filtrate contained phosphoric acid in amount sufficient to permit its recognition by molybdate, but there was not enough to determine.

Even in the absence of an excess of magnesium chloride the phosphoric acid is wholly precipitated, although ammonium chloride may be present in large amount. The precipitate thus obtained is, however, never of the correct composition. It invariably contains an excess of phosphoric acid and this excess is proportional to the amount of sal ammoniac present. This error is not counteracted by the presence of an amount of magnesium chloride sufficient to form a precipitate of the proper composition.

In the presence of an excess of magnesium chloride the precipitate invariably contains at least enough magnesia to form the normal salt, even in the presence of an excess of ammonium salts. A pure precipitate is, however, only obtained when the amount of free ammonia present is just sufficient for its formation. Any excess of the base causes the precipitate to contain too much magnesia. When ammonia is allowed to slowly flow into a solution containing phosphoric acid and a magnesium salt in excess, the precipitate formed has the normal composition, provided that the rate of flow has been so regulated that the precipitation has taken place in neutral solution. Of course an excess of ammonia must be finally added in order to secure complete precipitation, but this excess is not injurious after the precipitate has once formed.

Various attempts were made to secure a process giving reliable results and yet not too clumsy for practice. Ammoniacal solution of phosphomolybdic acid was neutralized with hydrochloric acid till the yellow precipitate no longer disappeared on stirring and no smell of ammonia could be detected, neutral magnesium chloride solution containing ammonium chloride added, and then dilute ammonia, till a precipitate began to appear. The solution was allowed to stand for awhile, a trifle more ammonia added, and finally, after another wait, an excess of ammonia. By this process correct results were occasionally obtained, but usually the precipitate was a trifle (0.0 to 1.5 mgms.) too heavy and gave Tollen's reaction. For many purposes the results are sufficiently close.

It is probable that in the presence of excess of magnesium chloride and of ammonia some trimagnesium phosphate is

formed, for it is not likely that the excess of magnesia in the precipitate is due to oxide mechanically carried down in the precipitate when quickly formed.

When hydrochloric acid is added to an ammoniacal solution of phosphomolybdate till the precipitate redissolves with difficulty on stirring, the solution reddens blue litmus paper and probably contains free phosphomolybdic acid. On now adding first magnesium chloride in excess and then ammonia, ammonium phosphomolybdate is probably first formed, and then this salt gradually breaks up as more ammonia is added, forming magnesium ammonium phosphate with the magnesia already in solution.

Precipitates obtained from solutions approximately neutral often contain noticeable proportions of molybdic acid in the free state. This is caused by the decomposition of phosphomolybdic acid by ammonia and magnesium chloride. As molybdic acid is not particularly soluble in water, it is deposited simultaneously with the magnesium ammonium phosphate and is enclosed by the latter salt to some extent, and so shielded from the solvent action of the excess of ammonia later added. This separation of free molybdic acid, of course, does not occur in the presence of free ammonia.

The difficulty of preparing the pure double phosphate is not so great in the absence of molybdate and when the excess of magnesium chloride is not large. Washed magnesian precipitates dissolved in hydrochloric acid containing a slight amount of magnesium chloride, and carefully reprecipitated with ammonia, gave better results than had been hitherto obtained. The process is, however, too dependent on the skill of the operator to be reliable.

Magnesium ammonium phosphate can be obtained in three different conditions:

(1) The precipitate is formed in neutral or ammoniacal solution containing no excess of magnesium salt. The result of this is that the precipitate contains less than the normal amount of magnesia, and phosphoric oxide is volatilized on ignition. Therefore weights come out too low.

(2) The precipitate is formed in the presence of an excess of

magnesium salt, but during its formation ammonia is not present in excess. As a result the precipitate possesses the normal constitution and the weights obtained are correct.

(3) The precipitate is formed in the presence of an excess of both ammonia and magnesium salts. The result is that the precipitate contains an excess of magnesia and the weights afforded are consequently too high.

Viewing in the light of these results the method for the precipitation of phosphoric acid (that of Abesser, Jani and Maercker), in which the ammoniacal solution of the yellow precipitate is approximately neutralized with hydrochloric acid, magnesia mixture then added, and subsequently an excess of ammonia, it is readily seen that the following sources of error exist:

A. The whole precipitate is formed as is indicated under (1). This occurs when the amount of ammonia present in the magnesia mixture is so large that precipitation of the phosphoric acid is at once effected when the reagent is slowly added and the liquid stirred, excess of magnesia not being present during the precipitation. Subsequent addition of excess of magnesium chloride or of ammonia is of no avail. The results are similar to those obtained by Wagner's process (in which the neutralization with hydrochloric acid is not practiced).

B. In the formation of the precipitate all three conditions successively occur. This is the case when the amount of ammonia in the magnesia mixture is such that when the reagent is added, drop by drop, stirring constantly, precipitation begins while there is no excess of magnesia, but continues after an excess has been added. Under these circumstances the errors may nearly balance. It is not practicable to form the precipitate wholly of the composition given under (2).

C. When magnesia mixture and ammonia are added drop by drop, stirring constantly, the precipitate formed generally has the composition given under (2) and (3). The 2.5 per cent. ammonia of the usual magnesia mixture is so weak that the precipitate begins to form when magnesia is in excess. The results are consequently too high, and the quicker the precipitation has been effected the higher the results are likely to be, from the

fact that a smaller portion of the precipitate is formed in neutral solution.

D. The precipitate is exclusively of the composition given under (3) only when magnesia mixture and ammonia are too quickly added. The results are in this case even higher than those just referred to under C.

These theoretical conclusions were confirmed by direct experiment.

The common citrate method gives approximate results which is due to the fact that two sources of error counterbalance each other. On the one hand the precipitate invariably contains lime and on the other the phosphoric acid is not completely precipitated. When magnesia mixture is slowly added to an ammoniacal solution of phosphoric acid containing ammonium citrate but no bases forming insoluble salts with phosphoric acid, the precipitate forms mostly in the condition given under (1) and but little in that given under (3), inasmuch as most of it is formed in the absence of an excess of magnesium chloride. This view was confirmed by experiment, but it was also shown that even when the magnesia was rapidly added, some phosphoric acid was volatilized during the subsequent ignition of the precipitate. This is due to the fact that from solutions of phosphoric acid containing no lime salts the precipitate is formed with tolerable rapidity even where citrate was present, so that on the addition of the magnesia mixture a portion of the precipitate is formed in the absence of an excess of magnesium chloride.

The general conclusion drawn from the results of a number of determinations made by various modifications of the molybdate method and by the citrate method is that none of these methods is particularly accurate. It appears practically impossible to completely convert phosphoric acid into pure magnesium pyrophosphate under analytical conditions, where the molybdate method is employed. The exact amount of phosphoric acid in a substance can therefore only be obtained by correcting the results analytically found by a factor, assuming that the errors of analysis are constant for a given amount of phosphoric acid.

Results obtained, where the neutralization with hydrochloric acid is practiced, are oftener nearer the truth than where this

precaution is omitted. However, results thus obtained are dependent on so many sources of error that it is difficult to make parallel analyses. Besides this the method is rather inconvenient. The molybdic acid occurring in the precipitate is a nuisance. Its complete removal by ignition requires skill and practice, and often as much time as the expulsion of the volatile phosphoric acid from the precipitate formed where neutralization is omitted (Wagner's modification). On the other hand the latter modification of the method is very convenient in practice and the attendant relations are so simple, that duplicates must agree where simple precautions are observed.

A systematic determination was made of the errors attendant on Wagner's method and from the results a table constructed, the use of which is recommended for phosphate determinations. The source of error in this method lies exclusively in the loss of phosphoric acid by volatilization. The magnesia-covered crucible lid offers a very good control of this error and its use is recommended to the analyst. Of course, the presence of sulphur in the gas used for ignition is liable to disturb this check.

The following course of procedure in the determination of phosphoric acid can be recommended:

Separate the phosphoric acid in the form of the yellow precipitate and wash this latter in the usual way. Too high a heat should not be employed, nor should the solutions be allowed to stand too long lest excess of molybdic acid separate. Dissolve the phosphomolybdate in 100 cc. of cold 2.5 per cent. ammonia and add as many cc. of the usual magnesia mixture (fifty-five grams magnesium chloride and seventy grams ammonium chloride dissolved in a liter of 2.5 per cent. ammonia) as there are centigrams of phosphoric acid present. Addition should not be made faster than ten cc. per minute. Stir during the addition. After the precipitation stir briskly once more and then allow to stand at least three hours. Wash with 2.5 per cent. ammonia till the chlorine reaction disappears, dry the filter and introduce into a well-cleaned crucible which has been thoroughly ignited. Place the lid at an angle, carbonize the filter and gradually raise the heat, though not higher than a medium red heat, till the pyrophosphate becomes completely white. When

this happens bring the blast into action and ignite to constant weight. The weight finally accepted must not change even after half an hour's ignition. Upon this requirement especial stress must be laid. Pure magnesium pyrophosphate does not suffer any loss even after several hours' ignition, nor does a good platinum crucible. To the weighed amount of pyrophosphate add the correction given in the table. Multiplication of the sum by 64 gives the amount of phosphoric acid in the weight taken for analysis.

CORRECTION FOR PHOSPHORIC ACID DETERMINATION.

| Found,
$\text{Mg}_2\text{P}_2\text{O}_7$,
in grams. | Lost,
milligrams
$\text{Mg}_2\text{P}_2\text{O}_7$. | Found,
$\text{Mg}_2\text{P}_2\text{O}_7$,
in grams. | Lost,
milligrams
$\text{Mg}_2\text{P}_2\text{O}_7$. |
|--|--|--|--|
| 0.10 | 0.6 | 0.24 | 4.0 |
| 0.12 | 0.8 | 0.25 | 4.2 |
| 0.14 | 1.2 | 0.26 | 4.6 |
| 0.15 | 1.4 | 0.27 | 5.0 |
| 0.16 | 1.6 | 0.28 | 5.5 |
| 0.17 | 2.4 | 0.29 | 6.1 |
| 0.18 | 2.6 | 0.30 | 6.8 |
| 0.19 | 3.2 | 0.31 | 7.6 |
| 0.20 | 3.5 | 0.32 | 8.6 |
| 0.21 | 3.6 | 0.33 | 9.6 |
| 0.22 | 3.8 | 0.34 | 10.6 |

When phosphoric acid is to be estimated as pyrophosphate it must always be first separated as molybdate, even when the original solution contained no bases capable of forming insoluble phosphates, as otherwise these corrections will not be applicable.

Using these corrections, the estimation of phosphoric acid becomes one of the most accurate of known analytical methods.

EXPERIMENTS ON A FERRO-TUNGSTEN.

BY JAMES S. DE BENNEVILLE.

Received February 28, 1894.

IN making an analysis of a ferro-tungsten rich in tungsten the chemical behavior of a residue insoluble in acids and apparently not decomposed by fused solvents led me to believe that it was metallic tungsten. The time available was limited and the few experiments made were hasty and at intervals, and in a private communication describing the method pursued in analy-

sis I called attention to the insufficient basis on which the analysis rested and the necessity for further investigation. The work involved in this paper was undertaken to determine, if possible, whether tungsten existed uncombined in the alloy and whether any definite ratio between tungsten and iron could be shown or alloys separated. The results showed that what was taken to be tungsten was a rich tungsten alloy the iron of which was not attacked by acids and which in its indifference toward chemical reagents resembled metallic tungsten.

The method of analysis adopted was directed toward determining how different solvents would act on the alloy. The steps taken were from the less to the more energetic reagent and consisted in 1. Attack by strong hydrochloric acid and determination of the iron and tungsten so removed in solution. 2. Fusion of the residue with a mixture of alkali carbonate and nitrate. 3. Action of solution of silver nitrate on the alloy.

The results based on sixteen analyses showed the alloy to be very heterogeneous. The sample was in the form of small fragments showing to the eye the differentiation throughout the mass and even the fragments themselves had not the same appearance, some of them having a number of cleavage planes of a pyritous appearance. In making these later analyses no effort was made to obtain a uniform sample, but the contrary, for the object sought was to ascertain whether all the iron was alloyed with tungsten or *vice versa*; and whether iron and tungsten were present as such dissolved in a true alloy.

A marked regularity was shown in the amount of tungsten dissolved on treating the alloy with ammoniacal silver nitrate solution. However, on digesting with neutral solution of silver nitrate no tungstic acid separated and the silver precipitated was in proportion to the iron dissolved. This absence of tungstic acid from the residue pointed to the fact that all the tungsten was in the form of alloy. The small quantity of iron separated did not calculate to any definite ratio with the tungsten acted on by the silver salt. Part of the iron was probably due to the steel mortar in which, owing to its great hardness, it was necessary to crush the alloy. This would vitiate any calculation.

The results, under I, were obtained by the following method: The fragments of the alloy were powdered separately in a steel mortar and passed through a sixty mesh sieve. Weighed portions were then extracted by strong hydrochloric acid (sp. gr. 1.20) until the acid no longer acted. In this solution iron and tungsten were determined. The residue was fused with a mixture of sodium carbonate and nitrate and the fusion lixiviated in water. Decomposition was complete. Iron and tungsten were determined. The results obtained were as follows:

I. TO ONE GRAM.

| No. | 1 | 2 | 3 | 4 |
|--------------------------|--------|--------|--------|--------|
| Acid extract, iron | 0.3648 | 0.3779 | 0.3631 | 0.3853 |
| Acid extract, tungsten.. | 0.0233 | 0.0309 | 0.0217 | 0.0282 |
| Residue, iron..... | 0.1786 | 0.1762 | 0.1669 | 0.1416 |
| Residue, tungsten..... | 0.4333 | 0.4057 | 0.4390 | 0.4626 |

Taken in connection with II this table appears to show that part of the alloy is readily attacked by acid, iron being dissolved and the tungsten left behind in the residue. This is indicated by the small quantity of free iron (see II) in the majority of the samples taken for analysis. Any large quantity of unalloyed iron would be shown very positively. This does not show necessarily the separation of an easily decomposed alloy from others less readily attacked. Other facts, given later, indicate that this alloy is an unsaturated compound and that a still higher percentage of tungsten than given in these analyses can be held chemically combined with the iron, but the higher valency exercised by the iron in these rich tungsten compounds may not be the most stable.

It was sought to ascertain how the alloy would act toward silver solution. Four reactions were involved. 1. Metallic iron, reducing silver from its salts in the ratio of Fe:2Ag. The reaction takes place in neutral solution. 2. Metallic tungsten and silver salt in neutral solution. 3. Metallic tungsten and silver salt in ammoniacal solution. 4. Action of the tungsten in this alloy on the silver salt. In the neutral solution of silver nitrate tungsten is converted into tungstic acid and silver is reduced. Silver tungstate is also formed. After washing the precipitated tungstic acid and silver free from excess of silver nitrate and dissolving in ammonia the black silver sulphide was obtained by

the separated and unalloyed iron would surround a rich tungsten alloy. Schneider¹ separated from a high tungsten iron what appeared to be two alloys corresponding to the formulas Fe_2W and Fe_3W . If iron be regarded as divalent the saturation point of tungsten would be reached in the formula Fe_2W (taking tungsten as hexavalent). If iron be regarded as octovalent the saturation formula would be Fe_3W_4 . Howe in his "Metallurgy of Steel" states that "tungsten unites with iron apparently in all proportions at least up to eighty per cent." The following table of analyses is taken from his work quoted, p. 81:

| No. | 1. | 2. | 3. | 4. | 5. | 6. |
|----------------|----|------|------|------------|-------|-------|
| Tungsten..... | 37 | 77.8 | 53.1 | 29.12 | 24.25 | 28.18 |
| Iron..... | 63 | 16.4 | 43.4 | 67.93 | 30. | 68.36 |
| Manganese..... | .. | 5.8 | 3.5 | but little | 41.50 | 0.99 |
| Silicon..... | .. | | | 0.61 | | 0.23 |
| Carbon..... | .. | | | 1.17 | 5.65 | 1.88 |
| Phosphorus.... | .. | | | | 0.14 | 0.008 |

The description given of No. 3, "platinum gray, hard, brittle, lamellar completely fusible" would in the first three qualities apply directly to the ferro-tungsten under consideration. Analysis No. 2 very closely approximates the formula Fe_2W_3 and if no alloy of iron and tungsten, in combination, containing a higher percentage of tungsten, exists, it would point strongly to the octovalency of iron in its combinations with this element as metal. The other analyses, including those of the ferro-tungsten under consideration would be unsaturated compounds. This valency has been shown to belong to other members of this family. Ruthenium and osmium in their oxides, iron in ferric acid, appear as hexavalent and the existence of the ammonia cobalt salts indicate a still higher valency for a metal closely allied to iron.²

Mendelejeff compares alloys to solutions as indefinite unstable compounds. In solutions in which there is free communication within the bounds of the liquid on alteration in temperature a change in molecular composition occurs as is shown by the separation of definite salts limited by such temperature. An alloy in the fused state is then analogous to a solution and when during

¹ Howe's Metallurgy of Steel, p. 81.

² Lothar Meyer, "Modern Theories of Chemistry," pp. 347, 348.

cooling segregation sets in the different alloys crystallize out from the mass. If the iron were present in such quantity that its saturation capacity for the tungsten would drop below divalency metallic iron would appear in this alloy but this is not the case.

The fact that iron does not replace silver in the silver nitrate or copper in the copper ammonium chloride shows a very strong affinity of iron for tungsten. If the bond between the iron and tungsten atoms was weak, or if there was merely a mechanical mixture, iron should replace silver in the neutral solution of the silver salt. This is based on the fact that "a positive element is separated from its combinations with a negative element by a stronger positive," and iron is more positive than silver.¹ Iron and tungsten are so separated in their properties as metal and semi-metal that an alloy of such constituents should be a very stable compound.

Metallic tungsten is left almost unattacked by hot acid. The action of aqua regia slowly converts it into tungstic acid. The acid must be used in small portions at a time and adhering tungstic acid removed by ammonia to prevent its protective action. Fusion with potassium bisulphate, or with caustic soda, or alkaline carbonate and saltpeter decomposes it.

In its action toward acids the alloy shows very strongly the influence of the tungsten. Acids do not act on it energetically as with carbon steel. To a degree this is to be expected but its inertness is almost as marked as with metallic tungsten. Hydrochloric acid dissolves out about two-thirds of the iron and a little tungsten. Nitric acid does the same. Part of the alloyed iron, therefore, appears to be attacked by acid solvents. Sulphuric acid barely acts upon it but fusion with potassium bisulphate (sulphuric acid at a red heat) decomposes the alloy completely. Aqua regia attacks it slowly but action is soon stopped by the tungstic acid forming a coating which must be removed to obtain further action on the alloy by the solvent. This chemical behavior points to a complex molecular structure. The formula Fe_2W_4 is purely empirical and the true formula is probably a very large multiple of this. If the fusibility and volatility of

¹ Modern Theories of Chemistry, pp. 515-517.

compounds diminishes with increasing complexity of structure then in such difficultly volatile metals as tungsten, chromium, platinum, and other metals fusing at high temperatures, and in their alloys, the molecule (in the solid state) must be possessed of large molecular weight and corresponding inertness toward chemical action.¹

I am indebted to Dr. Wahl, of Philadelphia, through Mr. Garrison, for the material on which these analyses were made.

THE DIRECT ESTIMATION OF CITRATE SOLUBLE PHOSPHORIC ACID.

By B. B. ROSS.

Received December 18, 1893.

THE direct determination of citrate soluble phosphoric acid, as is well known, is effected in many European laboratories by precipitating it, as magnesium ammonium phosphate in the presence of the ammonium citrate employed in effecting its solution.

The lack of general applicability, together with other objections, which have been urged against this method, however, has caused its employment to be somewhat restricted and the process has met with little favor in this country.

The presence of the citric acid in the solution has, of course, prevented the direct application of the molybdate method, and several processes have been proposed for the elimination of the citric acid preparatory to the precipitation of the phosphoric acid by the molybdate solution. The writer some years since (Proceedings Association Official Agricultural Chemists, 1885,) proposed the removal of the citric acid by precipitation in the hot solution by means of calcium chloride.

A number of results reported at that time showed quite a close agreement with the figures obtained by the regular official method, but some later tests indicated a loss resulting from the retention of small quantities of calcium phosphate in the precipitate of calcium citrate.

¹ "Modern Theories of Chemistry," pp. 131, 287. Ostwald "Outlines of General Chemistry," pp. 190, 191; in reference to potassium as solid p. 275.

Kuntze (*Ztschr. f. Rübenzucker*, 1892, 860,) recommends for the destruction of citric acid and other organic matters, evaporation of the solution and treatment with sulphuric and nitric acids, followed by thorough ignition. During the past year a number of experiments were made in the laboratory of the Louisiana State University with a view to the elimination of citric acid by means of oxidizing agents by the wet way.

After testing a number of different methods of oxidation it was found that the best and most satisfactory results were to be secured by the employment of the Kjeldahl digestion process. The mode of procedure finally adopted is essentially as follows:

After the completion of the thirty minutes' digestion of the sample with 100 cc. of citrate solution, twenty-five cc. of the liquid are at once filtered out into a dry vessel, preferably into a burette, as the solution can, after cooling, be transferred to another vessel without the dilution attendant upon rinsing the measuring vessel.

Bring the aliquot, thus measured, into a digestion flask of 250 to 300 cc. capacity, add about fifteen cc. concentrated sulphuric acid and place the flask on a piece of gauze over a moderately brisk flame.

Within about eight minutes the liquid will have become quite concentrated and will begin to darken appreciably and at the same time foaming will commence, but will occasion no trouble if an extremely high, or a very low flame be avoided.

After a further lapse of three or four minutes the foaming ceases and the contents of the flask appear quite black; about one gram of mercuric oxide or metallic mercury is now added and the digestion continued over a high flame.

The operation can be readily completed within less than half an hour, and, in many cases, within twenty-five minutes, a clear and almost colorless liquid being obtained.

After cooling, the solution is washed into a beaker, ammonia is added in slight excess, the solution acidified with nitric acid and the regular molybdate method followed, after addition of ammonium nitrate.

In case as large an amount as fifty cc. (corresponding to one gram of the sample) of the filtrate from the citrate treatment is

employed, ten cc. of strong sulphuric acid are at first added and the digestion conducted in a flask of 350 to 500 cc. capacity; after the contents of the flask have blackened and the foaming has progressed considerably, the flask is removed from the flame and fifteen cc. more of sulphuric acid are added and the flask and contents heated with a low flame for two or three minutes; mercuric oxide is next added and the digestion is completed as before described.

Among the chief advantages of this process for the determination of citrate soluble phosphoric acid may be enumerated the following:

1st.—It affords a quick and direct method for the estimation of that form of phosphoric acid which, together with the water soluble, constitutes what is termed "available" phosphoric acid, and the amount of this available phosphoric acid is thus reached by two determinations instead of three according to the ordinary method.

2nd.—The economy of time and labor attendant upon this process gives it an advantage over the indirect method, since by the direct method it is only necessary to filter out twenty-five cc. (or possibly fifty cc.) of the citrate solution, thus obviating the frequently tedious task of filtering the whole liquid and bringing upon the filter and washing with water of a definite temperature the insoluble residue; in addition, the ignition of this residue, the subsequent digestion with acid, dilution to a definite volume and measurement of an aliquot, are operations which are either tedious or time-consuming and can to a large extent be avoided by the use of the direct process.

3rd.—If it is desired, this method can be used as a check or control process in connection with the regular method, the check determination being readily executed without the necessity of weighing a fresh quantity of the sample under examination.

The results of a number of comparative tests of this process and the regular official method are herewith inserted, the principal portions of the work reported having been performed by Mr. R. E. Blouin, assistant chemist, during the past fertilizer season.

The samples tested were ordinary commercial fertilizers and

it will be observed that the agreement in the figures obtained by the two processes is, in the main, quite close.

RESULTS OF CITRATE-SOLUBLE DETERMINATIONS.

| Sample No. | | By the direct
method. | By difference,
(Official method). |
|------------|---------|--------------------------|--------------------------------------|
| 1..... | | 2.16 | 2.16 |
| " " | 2..... | 5.63 | 5.67 |
| " " | 3..... | 5.37 | 5.39 |
| " " | 4..... | 2.44 | 2.64 |
| " " | 5..... | 2.00 | 1.86 |
| " " | 6..... | 5.40 | 5.33 |
| " " | 7..... | 6.90 | 6.78 |
| " " | 8..... | 4.55 | 4.51 |
| " " | 9..... | 2.75 | 2.73 |
| " " | 10..... | 2.04 | 1.98 |
| " " | 11..... | 2.07 | 2.09 |
| " " | 12..... | 6.46 | 6.48 |
| " " | 13..... | 5.24 | 5.11 |
| " " | 14..... | 5.12 | 5.06 |
| " " | 15..... | 2.87 | 2.91 |
| " " | 16..... | 1.61 | 1.53 |
| " " | 17..... | 0.37 | 0.33 |
| " " | 18..... | 0.94 | 0.90 |
| " " | 19..... | 0.33 | 0.36 |

In order to further test the reliability of the method, a solution containing phosphoric acid derived from a chemically pure phosphate was employed and phosphoric acid in the aqueous solution was determined by the regular molybdate method; a given quantity of the same solution was next mixed with twenty-five cc. of ammonium citrate solution and after addition of fifteen cc. sulphuric acid, the digestion was conducted as before described and the phosphoric acid determined in the manner previously stated. The results were:

By first method (direct molybdate process) 8.06 per cent.

By second method (addition of citrate solution, etc.) 8.13 per cent.

Other tests with chemically pure salts showed differences which were well within the limits of variation permissible in ordinary analytical work.

Experiments were also made with employment of potassium nitrate in the place of mercuric oxide, but it was found that a number of additions of this substance was required and the time

needed for the completion of the digestion was considerably lengthened.

The Gunning modification of the Kjeldahl digestion process was also tested but the foaming resulting from the employment of the large quantities of potassium sulphate rendered the use of this modification impracticable.

By the employment of either mercuric oxide or metallic mercury, however, the oxidation is effected rapidly and completely and the subsequent precipitation of the phosphoric acid is easily accomplished.

NOTES ON THE ESTIMATION OF CRUDE FIBER IN SUGAR CANE.

BY J. L. BEESON, PH.D., PROFESSOR OF CHEMISTRY, LOUISIANA SUGAR SCHOOL,
NEW ORLEANS.

Received February 26, 1904.

THERE is no part of the analytical work connected with the chemical control of diffusion process sugar house so unsatisfactory as that of the estimation of the so-called "crude fiber" in the cane, or that portion of the stalk which is insoluble in water. Duplicate analyses, manipulated with great care, show wide variations. The average of such variations for 100 samples taken consecutively was 0.736 per cent. Since the percentage of fiber is used as a factor in calculating the percentage of sucrose on the weight of the cane it becomes highly desirable that either a better method of fiber estimation be devised, or a more accurate and quick method of estimating the percentage of the sucrose directly on the weight of the cane. After a systematic and thorough investigation of the subject I have come to the conclusion that a very accurate method of fiber estimation for technical purposes is not feasible, on account of the wide variation in fiber content in different parts of the cane stalk.

Extraction of the Soluble Bodies from the Chips.—A study was first made of the extraction of the sugars and other soluble bodies in the chips as follows: Twenty grams of chips taken from the comminuter were placed in a beaker, and nine volumes of water of varying temperatures added. The diffusates were polarized every fifteen minutes until the last two readings were the same.

The water in the beakers was kept as nearly as possible at the temperature of the water when added.

Results:

| | | | |
|----|------------|-----------------------|-------------|
| At | 23° C., | diffusion complete in | 65 minutes. |
| " | 60° C., | " | " 45-50 " |
| " | 75-80° C., | " | " 30-35 " |

After pouring off the diffusate as completely as possible the above process was repeated in order to see if there was any appreciable difference in the rate of diffusion for the second application of water, but there was none.

From the polariscope readings of the completely diffused solutions the percentage of extraction of sucrose was calculated for the first two applications of water, and found to be seventy-five to eighty-five per cent. Assuming eighty per cent. for the average of each application of water, and twelve per cent. as the average amount of sucrose in the chips, after five complete diffusions of each sample there would remain in the chips only 0.0384 per cent. of sucrose, which is practically nil. Theoretically, ninety per cent. of the sucrose should be removed for each complete diffusion. In quite a number of cases the final diffusate was tested for sugars by means of the α naphthol reaction, which invariably showed only a very low percentage of these bodies.

The coagulation point of the water soluble albuminoids by heat was ascertained by gradually raising the temperature of the first diffusates till coagulation began, and found to be between 80 and 90° C. It is therefore unnecessary to begin the extraction by the addition of cold water, then warm water, etc., as is usually done. Since the diffusion is so much more rapid at high temperatures it is advantageous to begin by adding water at 75° C. for the first two diffusions, and boiling water for the last three, letting stand each time for thirty minutes. This can be safely done, as it will be seen, without fear of coagulating the albuminoids. This method was followed throughout the season.

Losses in the Preparation of the Samples.—In preparing samples for the estimation of the fiber in different parts of the cane, a portion of a cane stalk cut at the internodes with a sharp knife was rapidly weighed, ten grams cut off from both ends into a tared beaker, and the stalk reweighed, and was found to sus-

tain a greater loss than the ten grams cut off. This process was repeated in four cases, giving similar results.

Results:

| | | |
|--------|---|--------|
| No. 1. | Difference in weight after cutting off ten grams, | 10.113 |
| " 2. | " " " " " " " " | 10.161 |
| " 3. | " " " " " " " " | 10.100 |
| " 4. | " " " " " " " " | 10.102 |

The chips were cut off in semi-circular pieces about $\frac{1}{8}$ of an inch in diameter. Sample 1, as soon as weighed, was cut finer with a pair of sharp scissors and rapidly weighed. It sustained a further loss of 0.107 gram, which added to the first loss makes a total of 0.22 per cent. while preparing the sample. These losses could not have been due in the main to evaporation, for the whole time occupied in preparing sample No. 1 was not over twenty minutes. Then Nos. 2, 3, and 4, were cut off early in the morning when the samples of 10 grams each lost by evaporation, for one hour, on an average 0.079 gram. The loss was more likely a mechanical one of the juice due to the rupture of the cells by the knife while cutting off the chips. If so, this loss would be augmented by the cutter and comminuter in the mill, especially so when the knives are dull.

Loss by Evaporation from the Chips.—According to well-known laws of physics the amount of evaporation varies with time of exposure, surface area exposed, and the temperature and humidity of the atmosphere. The fineness of the chips, which increases the surface, affects the rate of evaporation, probably also the ratio of the juice to the fiber. Upon the latter point I made no experiments. A piece of cane stalk, about an inch in diameter, was cut at the internodes, weighed, placed in the shade and reweighed at the end of each hour. The temperature at 12 o'clock 78° F., day dry.

Results:

| | |
|--------------------------------------|------------|
| 12-1 P. M., loss by evaporation..... | 0.48 gram. |
| 1-2 " " " " | 0.56 " |
| 2-3 " " " " | 0.40 " |
| 3-4 " " " " | 0.49 " |
| 4-5 " " " " | 0.52 " |
| Average loss each hour..... | 0.49 gram. |

This evaporation was mainly from the open ends and is therefore largely independent of the length of the piece of stalk.

Ten grams of chips were placed in a beaker in the room and weighed every hour, with the following results:

| | | | |
|--------|-------------------------|----------------------|-------------|
| No. 1. | From 10.30-11.30 A. M., | loss by evaporation, | 0.086 gram. |
| " 2. | " " " " " " | " " " | 0.073 " |
| " 1. | " 11.30-12.30 " " " | " " " | 0.269 " |
| " 2. | " " " " " " | " " " | 0.266 " |

The morning was very damp, there being a heavy fog which did not clear away until nearly 10 o'clock. From these results it would appear that quite an error may come from evaporation of the chips while the samples are accumulating at the mill, which often requires an hour or more. Add to this the mechanical loss from cutting the chips by the machine, and the error is sufficient to make the fiber appreciably high.

The Distribution of Fiber in the Cane.—These sources of error do not, of course, account for the differences in duplicate analyses. This error must be sought for in the difficulties in obtaining an average sample—in the variation in the fiber content in the different parts of the cane. To this end the following analyses were made: Ten grams of fiber were cut from the nodes, and ten grams from the contiguous internodes of the top, middle and butt of a stalk of purple cane, third year stubble of average size and weight, and the fiber estimated in these portions, giving the following results:

| | | | |
|--------|---------------------------|----------|--------------------------|
| Top { | Node..... 15.86 per cent. | Middle { | Node..... 15.9 per cent. |
| | Internode 8.60 " " | | Internode 8.0 " " |
| Butt { | Node..... 18.20 per cent. | | |
| | Internode 8.08 " " | | |

It will be noticed that there is approximately twice the percentage of fiber in the nodes as in the internodes, the butt node showing the highest percentage.

Fiber content in the rind and pulp of portions of cane stalk taken from the top, middle, and butt, cut so as to include a node and internode. (a) purple variety, plant cane; (b) purple variety, third year stubble.

| | Rind. | Pulp. | | Rind. | Pulp. |
|--------------|-------|-------|--------------|-------|-------|
| (a) Top..... | 26.0 | 8.7 | (b) Top..... | 25.6 | 7.80 |
| Middle .. | 29.5 | 6.5 | Middle.. | 28.5 | 5.40 |
| Butt | 28.5 | 6.8 | Butt..... | 28.5 | 5.77 |

Stubble cane always has a higher fiber content than plant cane of the same variety. From the above it would appear that this difference resides more in the pulp than in the rind.

It is difficult to say just what is rind and what is pulp in the cane stalk. So a portion of cane, about five inches in length, was cut from the center of a stalk of plant cane, purple variety, just within the two nodes. Ten grams of the rind was pared off into one beaker, ten grams taken off all round from what remained, and so on until the center of the stalk was reached, and the fiber estimated in these separate portions with the following results:

| | | |
|----------------------------------|-------|-----------|
| True rind | 33.9 | per cent. |
| Inside rind or bast tissue | 13.33 | " " |
| Next to inside rind | 6.79 | " " |
| Next to middle | 4.77 | " " |
| Middle | 4.13 | " " |

The diffusate from the inside bark (bast cells?) was quite yellow, and it is probable that these cells furnish the yellow coloring matter in the expressed juice.

A joint of cane was cut just without the nodes, and the true node separated from that portion penetrated by the rootlets of the eye. Then ten grams were cut off from both ends of what remained at right angles to the length of the stalk, and an average of what remained was taken, and the fiber estimated in these portions, with the following results:

PURPLE VARIETY, THIRD YEAR STUBBLE.

| | | |
|---------------------------|-------|-----------|
| Nodes proper | 21.3 | per cent. |
| Root nodes | 14.2 | " " |
| Next to the above | 14.13 | " " |
| Remaining internode | 11.9 | " " |

From the above data it will be seen that the fiber varies very widely in amount in different parts of the cane, from 4.13 per cent. in the pulp to 33.9 per cent. in the rind. The percentage of what was considered as rind in the above analyses was estimated, and as an average of four cases was approximately twenty-one per cent. the weight of the cane. With such a difference in the fiber content of the rind and pulp, and such a percentage of rind, it is no small wonder that the duplicate analyses could not be brought to agree. For the presence of a very small undue proportion of rind or pulp in the samples would make the duplicates disagree. Often the knives of the cutters are dull, and strips of rind, varying in length, get into the chips. These, by the motion of the carriers, tend to accumulate on top, and are easily gotten hold of in undue proportion in the taking of the

sample. In such cases it is more difficult to get an average sample than when the chips are fine and regular.

LOSS OF GOLD AND SILVER DURING SCORIFICATION ASSAY.

BY W. P. MASON AND J. W. BOWMAN.

Received October 6, 1893.

NO explanation of the following numerical results is required, beyond stating that the losses referred to represent total losses, that is to say, losses due to both volatilization and mechanical causes. The furnaces employed were "Battersea No. F," and the conditions under which the assays were made, such as heat of muffle, draught in muffle, and manipulations in general, were such as would obtain in careful practical work.

| SILVER. | | | | GOLD. | | | |
|----------------------------------|-------------------------|------------------------|-----------|-----------------------------------|-------------------------|------------------------|-----------|
| Weight before cupelling. | Weight after cupelling. | Loss. | Per cent. | Weight before cupelling. | Weight after cupelling. | Loss. | Per cent. |
| 210.765 | 206.360 | 4.405 | 2.09 | 338.030 | 335.025 | 3.005 | 0.888 |
| 543.165 | 535.645 | 7.52 | 1.38 | 349.020 | 348.200 | 0.820 | 0.234 |
| 206.360 | 200.325 | 6.035 | 2.92 | 335.025 | 334.365 | 0.660 | 0.197 |
| 535.645 | 523.330 | 12.315 | 2.29 | 348.200 | 346.900 | 1.30 | 0.373 |
| 200.325 | 196.720 | 3.605 | 1.79 | 334.365 | 333.120 | 1.245 | 0.372 |
| 523.330 | 514.765 | 8.565 | 1.63 | 346.900 | 345.790 | 1.11 | 0.319 |
| 196.720 | 191.733 | 4.987 | 2.53 | 332.575 | 331.725 | 0.85 | 0.255 |
| 514.765 | 503.950 | 10.815 | 2.10 | 345.790 | 344.15 | 1.64 | 0.474 |
| 191.733 | 187.820 | 3.913 | 2.03 | 331.725 | 330.600 | 1.125 | 0.338 |
| 434.180 | 424.925 | 9.255 | 2.13 | 344.965 | 344.265 | 0.70 | 0.202 |
| 187.820 | 184.525 | 3.295 | 1.80 | 330.600 | 329.900 | 0.70 | 0.211 |
| 424.925 | 419.975 | 4.95 | 0.95 | 334.650 | 343.960 | 0.69 | 0.206 |
| 184.525 | 180.560 | 3.965 | 2.14 | 329.900 | 329.130 | 0.77 | 0.233 |
| 419.975 | 410.430 | 9.545 | 2.27 | 220.635 | 220.200 | 0.435 | 0.197 |
| 410.430 | 403.365 | 7.075 | 1.72 | 329.130 | 328.860 | 0.27 | 0.082 |
| 403.365 | 394.550 | 8.815 | 2.18 | 220.200 | 219.835 | 0.365 | 0.165 |
| Average loss..... 1.99 per cent. | | | | Average loss..... 0.296 per cent. | | | |
| " | " | entire process.. 2.54 | " " | " | " | entire process 0.87 | " " |
| " | " | by cupellation.. 1.99 | " " | " | " | by cupellation 0.296 | " " |
| " | " | in scorification. 0.55 | " " | " | " | in scorification 0.574 | " " |

| SILVER. | | | | GOLD. | | | |
|--|--|--------|-----------|--|--|-------|-----------|
| Weight before scorifying and cupelling. | Weight after scorifying and cupelling. | Loss. | Per cent. | Weight before scorifying and cupelling. | Weight after scorifying and cupelling. | Loss. | Per cent. |
| 466.850 | 453.200 | 13.65 | 2.92 | 357.750 | 351.982 | 5.768 | 1.61 |
| 480.052 | 469.575 | 10.477 | 2.18 | 388.525 | 382.565 | 5.960 | 1.53 |
| 455.00 | 434.365 | 20.635 | 4.53 | 353.782 | 346.234 | 7.548 | 2.10 |
| 471.375 | 456.475 | 14.9 | 3.16 | 384.365 | 382.033 | 2.332 | 0.60 |
| 436.165 | 425.780 | 10.385 | 2.38 | 348.034 | 346.325 | 1.709 | 0.49 |
| 458.275 | 448.818 | 9.457 | 2.06 | 383.833 | 381.875 | 1.958 | 0.51 |
| 427.580 | 418.533 | 9.057 | 2.11 | 348.125 | 346.435 | 1.690 | 0.48 |
| 652.350 | 641.520 | 10.83 | 1.66 | 478.120 | 471.920 | 6.2 | 1.29 |
| 354.200 | 344.520 | 9.68 | 2.73 | 348.235 | 346.250 | 1.985 | 0.57 |
| 643.320 | 628.175 | 15.155 | 2.35 | 473.720 | 471.225 | 2.495 | 0.52 |
| 346.320 | 340.500 | 5.82 | 1.68 | 348.05 | 346.465 | 1.585 | 0.45 |
| 614.920 | 600.565 | 14.355 | 2.33 | 356.425 | 352.435 | 3.99 | 1.11 |
| 342.300 | 333.075 | 9.225 | 2.69 | 348.265 | 345.535 | 2.73 | 0.78 |
| 602.365 | 592.200 | 10.165 | 1.68 | 354.235 | 352.525 | 1.71 | 0.48 |
| 334.875 | 327.140 | 7.735 | 2.30 | 347.335 | 345.800 | 1.535 | 0.44 |
| 594.000 | 581.465 | 12.535 | 2.11 | 354.325 | 352.075 | 2.25 | 0.63 |
| 328.84 | 317.83 | 11.11 | 3.37 | 347.600 | 344.135 | 3.465 | 0.99 |
| 567.62 | 555.365 | 12.255 | 2.15 | 353.875 | 350.925 | 2.95 | 0.83 |
| 219.450 | 210.765 | 8.685 | 3.95 | 221.635 | 219.25 | 2.385 | 1.07 |
| 557.165 | 543.165 | 14.000 | 2.51 | 352.725 | 349.02 | 3.705 | 1.05 |
| Average percentage loss.....2.54 per cent. | | | | Average percentage loss.... 0.87 per cent. | | | |

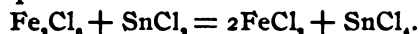
RENSSELAER POLYTECHNIC INSTITUTE,
1893.

ON THE SPEED OF REDUCTION OF FERRIC CHLORIDE BY STANNOUS CHLORIDE.

BY LOUIS KAHLENBERG.

Received February 8, 1894.

THE reaction that takes place when ferric chloride is treated with stannous chloride in aqueous solution is expressed by the following equation :



This reaction goes on slowly enough at ordinary temperatures to admit of study from the standpoint of chemical dynamics. It was my purpose to investigate whether the reaction proceeds

in accordance with the law of mass action, as stated by Guldberg and Waage,¹ and how the speed of the reaction is affected by the presence of varying quantities of free hydrochloric acid.

Outline of Method of Experimentation.—Solutions of ferric chloride and stannous chloride of known strength were prepared. These were brought to a definite temperature by allowing them to stand in a bath. They were then quickly mixed (in equivalent proportions), and the mixture was kept at the same temperature in an atmosphere of carbon dioxide. At convenient times, samples were taken out with a pipette; these were quickly run into an excess of a saturated solution of mercuric chloride, which, by converting the unchanged stannous chloride into stannic chloride, according to the equation, $\text{SnCl}_2 + 2\text{HgCl}_2 = \text{SnCl}_4 + 2\text{HgCl}$, checked the reaction. The amount of ferrous chloride formed was then determined by means of a standard solution of potassium bichromate. In this process, the bichromate was added until a drop of the mixture on a white porcelain plate showed no longer a blue coloration when brought into contact with a drop of a dilute, freshly prepared solution of potassium ferricyanide.

Preparation of Solutions.—A decinormal solution of potassium bichromate was prepared by taking 4.913 grams of the pure salt to a liter. Its strength was verified by comparison with both ferrous ammonium sulphate and iron wire. 17.85 cc. of this solution will change 0.1 gram of iron from the ferrous to the ferric state.

The ferric chloride used was of Merck's manufacture (C. P.). It was tested for arsenic and for sulphuric, nitric, and free hydrochloric acid, and found pure. Four liters of ferric chloride solution were prepared. The strength of this solution was determined by means of the decinormal bichromate solution, after previous reduction at a boiling heat with a slight excess of stannous chloride, and addition of an excess of mercuric chloride before titrating.² It was found that twenty-five cc. of the ferric chloride solution were equivalent to twenty-eight cc. of the bichromate.

¹ *Études sur les affinités chimiques*, 10, Christiania, 1867; also *J. prakt. Chem.*, [2], 19, 69.

² Kessler, *Pogg. Ann.*, 95, 223-225; also *Ztschr. anal. Chem.*, 11, 249.

Banca tin was used in preparing the solution of stannous chloride. The tin was found to be free from lead, iron, and arsenic. 30.5 grams of tin, to which a few scraps of platinum had been added, were heated with 125 cc. of hydrochloric acid of sp. gr. 1.17 in a flask in an atmosphere of carbon dioxide until nearly all the tin was dissolved. The heating had to be continued for about six hours. A little distilled water, previously boiled, was added from time to time so as to keep the volume of the liquid at about 100 cc. When the chemical action had ceased, about four to five grams of tin still remained undissolved. The excess of hydrochloric acid was driven off by boiling the liquid down to a small bulk. The stannous chloride thus obtained was diluted to 4,000 cc. with water previously boiled and cooled in an atmosphere of carbon dioxide. That the free hydrochloric acid had been driven off was evident from the fact that a precipitate of stannous oxychloride formed by diluting to this volume. It was found necessary to add to the four liters twenty cc. of hydrochloric acid, of sp. gr. 1.17, to bring this precipitate into solution. After this addition of acid and thorough shaking there still remained a faint opalescence, showing that a minimum quantity of acid had been used. The solution thus prepared was at once transferred to a number of flasks holding from 225 to 250 cc., about the quantity required for each series of experiments. The flasks were completely filled with the liquid, then tightly corked and kept in the dark. In this way the stannous chloride solution could be kept for weeks without changing, and the required quantity could be taken for use without exposing the remainder to the oxidizing influence of the air. The strength of the stannous chloride solution was determined as follows: Twenty-five cc. of the ferric chloride were acidified with hydrochloric acid and heated to boiling, twenty cc. of the stannous chloride were then quickly added and the amount of ferrous chloride formed at once estimated with the decinormal bichromate solution. In this way it was found that twenty cc. of the stannous chloride would reduce 18.7 cc. of the ferric chloride.

A saturated solution of mercuric chloride was also prepared.

Experimental Details.—In each of the six series of experiments

conducted, 200 cc. of the solution of stannous chloride and 187 cc. of the ferric chloride solution were used. The volume of this mixture was made up to 425 cc. for each series. In series I this was done by adding thirty-eight cc. of water, while in series II to VI, five, ten, fifteen, twenty, and twenty-five cc. of hydrochloric acid, of sp. gr. 1.17, at 20° C. respectively were added, together with an amount of water sufficient to make the volume up to 425 cc.

Preliminary experiments had shown that the speed of the reaction is greatly increased by raising the temperature and by increasing the amount of free hydrochloric acid present. The experiments were consequently carried out at 0° C., in order that the reaction might go on slowly enough to admit of the study of the increase of the speed of the reaction by the presence of the amounts of free hydrochloric acid above mentioned.

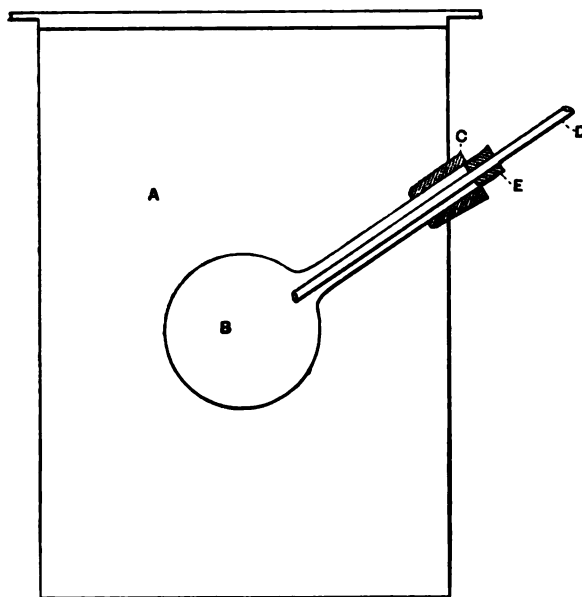


FIGURE 1.

Fig. 1 shows the apparatus in which the mixture of stannous chloride and ferric chloride was kept at 0° C. and in an atmosphere of carbon dioxide. The outer vessel A is made of tin and

has a capacity of about sixteen liters. It is provided with a wooden jacket and cover. The flask B has a capacity of about 500 cc. It is held in position by the tightly fitting rubber cork C which fits closely into the spout with which A is provided. The cork E fits loosely into the neck of the flask. The tube D is connected with a carbon dioxide generator.

At the beginning of each series of experiments, A was completely filled with melting ice and the air in the flask displaced by carbon dioxide. In the meantime the 200 cc. stannous chloride solution and the 187 cc. of ferric chloride solution, plus the thirty-eight cc. water—or water plus acid—were cooling in separate flasks in a bath of melting ice. When the solutions had been cooled to 0° C., they were quickly mixed and poured into the flask B, Fig. 1, the cork E being at once replaced. Samples of twenty-five cc. each were then taken out with a pipette from time to time, the cork E being slightly raised for the moment so that the pipette could be introduced into the flask B. These samples were quickly run into Erlenmeyer flasks containing fifteen cc. of the saturated mercuric chloride solution. The ferrous chloride formed was then estimated by means of the decinormal solution of potassium bichromate, the end of the reaction being judged as above stated. The results of the six series of experiments are given below.

Presentation of Results.—In accordance with the law of Guldberg and Waage, the speed of the reduction of ferric chloride by stannous chloride, when the substances are present in equivalent proportions, is to be expressed by the following equation:

$$\frac{dx}{dt} = c(a - x)^2, \quad (1)$$

in which a represents the amount of substance present at the outset, x , the amount of substance changed during the time, t , and c , a constant depending on the concentration, temperature, etc.

From the above equation we have by integration:

$$\frac{1}{a - x} = ct + K. \quad (2)$$

Determining K from the fact that x is zero when t is zero, and substituting its value in (2), we have after easy transformation,

$$\frac{I}{t} \frac{x}{a-x} = ac. \quad (3)$$

The condition then that must be fulfilled, if the reaction follow the law, is that ac be constant.

The results of the six series of experiments are given in tabular form. Under t is given the time in minutes, counted, in the case of series I to V, from ten minutes after mixing the substances; while in series VI, five minutes after mixing was taken as the zero point from which to count the time. In the second column are given the amounts of the decinormal bichromate solution used in estimating the ferrous chloride formed. In series I the results of the titrations of two independent series of experiments are given under 1 and 2, while the average is given under 3. The last three columns of each series give the values of x , $\frac{x}{a-x}$, and ac , respectively.

For purposes of comparison, the results given in series I to VI have also been charted in the form of curves—Fig. 2. The abscissae represent the time in minutes, counting from the time of mixing, and the ordinates represent the amounts of ferric chloride reduced in percentages of the total amount present at the beginning. The numbers of the curves correspond to the numbers of the series.

SERIES I. (No free HCl present.)

| t
(minutes.) | K ₂ Cr ₂ O ₇
(cc.) | | | x | $\frac{x}{a-x}$ | ac. |
|-----------------|--|------|------|------|-----------------|---------|
| | 1 | 2 | 3 | | | |
| 0..... | 1.3 | 1.25 | 1.27 | ... | | |
| 10..... | 2.1 | 2.3 | 2.2 | 0.93 | 0.0921 | 0.00921 |
| 20..... | 2.9 | 2.8 | 2.85 | 1.58 | 0.1672 | 0.00836 |
| 40..... | 3.7 | 3.7 | 3.7 | 2.43 | 0.2825 | 0.00706 |
| 60..... | 4.2 | 4.2 | 4.2 | 2.93 | 0.3617 | 0.00603 |
| 80..... | 4.8 | 4.6 | 4.7 | 3.43 | 0.4513 | 0.00564 |
| 100..... | 5.25 | 5.2 | 5.23 | 3.96 | 0.5601 | 0.00560 |
| 120..... | 5.6 | 5.6 | 5.6 | 4.33 | 0.6462 | 0.00539 |
| 140..... | 6.0 | 6.0 | 6.0 | 4.73 | 0.7508 | 0.00536 |
| 190..... | 6.6 | 6.4 | 6.5 | 5.23 | 0.9017 | 0.00475 |
| 250..... | 7.25 | 7.3 | 7.27 | 6.00 | 1.1928 | 0.00477 |
| 320..... | 7.6 | 7.6 | 7.6 | 6.33 | 1.3468 | 0.00421 |

(a = 11.03)

LOUIS KAHLBERG. ON THE SPEED OF

SERIES II. (Five cc. HCl present.)

| t
(minutes.) | K ₂ Cr ₂ O ₇
(cc.) | x | $\frac{x}{a-x}$ | ac. |
|-----------------|--|------|-----------------|---------|
| 0..... | 2.95 | ... | | |
| 10..... | 4.45 | 1.50 | 0.1911 | 0.01911 |
| 35..... | 6.55 | 3.60 | 0.6261 | 0.01789 |
| 50..... | 7.1 | 4.15 | 0.7981 | 0.01596 |
| 70..... | 7.6 | 4.65 | 0.9894 | 0.01413 |
| 80..... | 7.95 | 5.00 | 1.1494 | 0.01437 |
| 110..... | 8.5 | 5.55 | 1.4605 | 0.01327 |
| 140..... | 8.95 | 6.00 | 1.7910 | 0.01279 |
| 170..... | 9.3 | 6.35 | 2.1166 | 0.01245 |

(a = 9.35)

SERIES III. (Ten cc. free HCl present.)

| t
(minutes.) | K ₂ Cr ₂ O ₇
(cc.) | x | $\frac{x}{a-x}$ | ac. |
|-----------------|--|------|-----------------|--------|
| 0..... | 5.55 | ... | | |
| 10..... | 7.1 | 1.55 | 0.2981 | 0.0298 |
| 20..... | 7.95 | 2.40 | 0.5517 | 0.0276 |
| 30..... | 8.5 | 2.95 | 0.7763 | 0.0259 |
| 40..... | 8.95 | 3.40 | 1.0149 | 0.0254 |
| 50..... | 9.2 | 3.65 | 1.1778 | 0.0236 |
| 70..... | 9.65 | 4.10 | 1.5094 | 0.0216 |
| 100..... | 9.95 | 4.40 | 1.8734 | 0.0187 |
| 120..... | 10.15 | 4.60 | 2.1394 | 0.0178 |
| 150..... | 10.45 | 4.90 | 2.6487 | 0.0177 |

(a = 6.75)

SERIES IV. (Fifteen cc. free HCl present.)

| t
(minutes.) | K ₂ Cr ₂ O ₇
(cc.) | x | $\frac{x}{a-x}$ | ac. |
|-----------------|--|------|-----------------|--------|
| 0..... | 7.1 | ... | | |
| 10..... | 8.5 | 1.4 | 0.368 | 0.0368 |
| 20..... | 9.25 | 2.15 | 0.705 | 0.0352 |
| 30..... | 9.7 | 2.6 | 1.000 | 0.0333 |
| 40..... | 10.05 | 2.95 | 1.311 | 0.0328 |
| 50..... | 10.35 | 3.25 | 1.667 | 0.0333 |
| 70..... | 10.6 | 3.5 | 2.059 | 0.0292 |
| 80..... | 10.75 | 3.65 | 2.355 | 0.0294 |
| 90..... | 10.85 | 3.75 | 2.586 | 0.0287 |

(a = 5.2)

SERIES V. (Twenty cc. free HCl present.)

| t
(minutes.) | K ₂ Cr ₂ O ₇
(cc.) | x | $\frac{x}{a-x}$ | ac. |
|-----------------|--|------|-----------------|--------|
| 0..... | 7.55 | ... | | |
| 10..... | 9.15 | 1.6 | 0.508 | 0.0508 |
| 21..... | 9.95 | 2.4 | 1.021 | 0.0486 |
| 50..... | 10.8 | 3.25 | 2.167 | 0.0433 |
| 70..... | 11.1 | 3.55 | 2.958 | 0.0423 |
| 95..... | 11.35 | 3.8 | 4.000 | 0.0421 |

(a = 4.75)

SERIES VI. (Twenty-five cc. free HCl present.)

| t
(minutes.) | K ₂ Cr ₂ O ₇
(cc.) | x | $\frac{x}{a-x}$ | ac. |
|-----------------|--|------|-----------------|--------|
| 0..... | 7.05 | ... | | |
| 10..... | 9.25 | 2.2 | 0.721 | 0.0721 |
| 20..... | 10.15 | 3.1 | 1.442 | 0.0721 |
| 25..... | 10.40 | 3.35 | 1.763 | 0.0705 |
| 35..... | 10.75 | 3.7 | 2.387 | 0.0682 |
| 50..... | 11.00 | 3.95 | 3.038 | 0.0608 |
| 70..... | 11.25 | 4.2 | 4.000 | 0.0571 |
| 100..... | 11.45 | 4.4 | 5.176 | 0.0518 |
| 130..... | 11.55 | 4.5 | 6.081 | 0.0468 |

(a = 5.25)

It will be noticed that the quantity ac, instead of being constant, decreases in each series. In eight preliminary series of experiments, performed at 0° and at 15° to 16°, the same regular decrease of ac was noted. The cause of this retardation of the speed of the reaction has not been further investigated. It seems probable that it is due to the accumulation of the products of the reaction (stannic chloride and ferrous chloride), and to the change in the rate of diffusion as the solution becomes more dilute. It must be observed, however, that while the first values of ac in each of the six series given above are too high, owing probably to disturbing influences at the beginning of the experiments, the values at about the middle of the series vary but slightly indeed, in many instances the differences fall within the limit of error of experimentation. The results above given are sufficient to show that the reaction follows the law of Guldberg and Waage fairly well.

The effect of the presence of varying quantities of free hydrochloric acid on the speed of the reaction can best be seen by comparing the curves in Fig. 2. All the curves show that the reaction goes on most rapidly during the first ten to fifteen minutes after mixing.¹ During the first forty minutes after mixing, the second five cc. hydrochloric acid (curve III) increases the amount of ferric chloride reduced in about the same degree as does the first five cc. (curve II); but this effect diminishes relatively as the time increases. In general, the curves show that as the amount of free hydrochloric acid is increased the effect on

¹ This effect has in part been eliminated in preparing the tables above, by choosing ten minutes after mixing as the zero point from which to count the time.

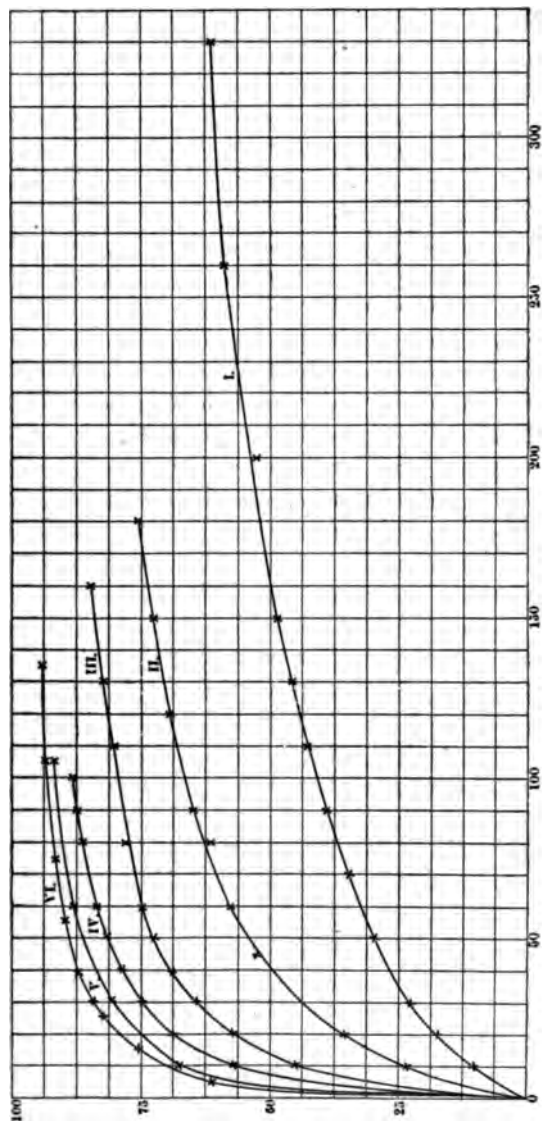


FIGURE 2.

Abscissae = Time in minutes.
 Ordinates = Amount of FeCl_3 reduced in per cent.

Curve I, no free HCl is present.
 " II, 5 cc. free HCl is present.
 " III, 10 " " " "
 " IV, 15 " " " "
 " V, 20 " " " "
 " VI, 25 " " " "

amount of ferric chloride reduced is relatively diminished.

Curves similar to those in Fig. 2 have lately been obtained by Seubert and Dorrer¹ in the case of the action of ferric chloride on potassium iodide. Their curves show the effect of the presence of an excess of either substance on the speed of the reaction.

In the case of the reduction of ferric chloride by stannous chloride, the part played by the free hydrochloric acid cannot be expressed in the form of a chemical equation; and as there can be no doubt that the amount of free acid present at the end of the reaction is the same as at the beginning, the action of the acid is catalytic in its nature. In the course of his investigations of processes of oxidation and reduction, Prof. Ostwald² has formulated the law that the speed of all processes of oxidation and reduction is increased by the presence of free acids in proportion to their affinity coefficients. He has shown that this law holds also in cases of catalytic action. It would be of interest in this connection to know the effect of the presence of equivalent quantities of other acids on the speed of the reduction of ferric chloride by stannous chloride; but as another problem required my immediate attention, the work could not be continued in this direction.

My thanks are due to Prof. W. W. Daniells for occasional helpful suggestions during the progress of the above experiments.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF WISCONSIN.

THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(Continued from Page 286.)

BY THOMAS B. STILLMAN, PH.D.

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[TO BE CONTINUED.]

CREAM OF TARTAR SUBSTITUTES: THEIR CHEMISTRY AND ANALYSIS.

By W. E. WADMAN.

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TO make an intelligent analysis of any complex substance, the chemist must possess not only the requisite skill, but also a certain amount of knowledge of the material he is working with, in order that the bare analytical results may be correctly interpreted, and given their proper meaning in relation to the particular substance yielding them.

Among the substances with which the majority of practicing chemists appear to be little familiar, is the class of products known in trade under the generic name of cream of tartar substitutes.

Under this general name are included a great many acid powders which are used to replace cream of tartar in the manufacture of baking powders, self-raising flours, and also directly in baking, their function being always that of an acid to liberate carbonic acid gas from sodium bicarbonate.

All cream of tartar substitutes have the common feature that their active acid element is primarily monocalcium phosphate, ($\text{CaH}_4\text{P}_2\text{O}_8$), but in other respects they differ so widely in composition and function, that for convenience in considering them it is best to divide them into two primary classes or types.

The first class (hereafter referred to as class I) consists of goods prepared by treating calcium phosphate (in practice usually in the form of boneblack) with sufficient sulphuric acid to produce monocalcium phosphate and calcium sulphate, filtering off the sulphate, evaporating the solution of monocalcium phosphate to crystallization, mixing with starch, drying and grinding. The resulting product is chiefly a mixture of monocalcium phosphate with starch, but invariably contains a small amount of "free" or uncombined phosphoric acid (varying from one per cent. to six per cent. P_2O_5), and also a considerable quantity of insoluble phosphates, chiefly calcium but frequently iron and aluminum phosphates also. Tartar substitutes of this class are frequently known in trade as "Leached goods."

The other primary type (hereafter referred to as class II) differs from the preceding in method of manufacture, in chemical composition and also in its use and behavior.

The raw material is carefully prepared, pure white bone ash which is treated with the requisite amount of concentrated sulphuric acid, and the resulting mixture, monocalcium phosphate and calcium sulphate, is dried and ground without separation. Hence goods of this type contain a large amount of calcium sulphate, equivalent to the amount of sulphuric acid used in their preparation, and are frequently referred to as "sulphate of lime base" goods.

The essential difference between the two principal types is, that one is practically free from calcium sulphate, while the other contains a large amount of this salt.

Like class I the goods of the second class almost always contain a small amount of free phosphoric acid, and generally considerable quantities of insoluble phosphate, chiefly tricalcium. As a rule they contain very little starch, and frequently none at all.

With regard to this content of calcium sulphate in goods of the second class, it is a common mistake of chemists who are not familiar with these materials, to stigmatize it as an "adulteration," or "the result of careless or imperfect manufacture." Such statements are entirely erroneous, as the calcium sulphate is an essential part of the goods and has a very important influence on their action, as explained later.

A point to be noticed, which is a stumbling block to many chemists, is the simultaneous occurrence of free phosphoric acid and insoluble phosphates. It is usually supposed that these two substances in contact will at once react to produce monocalcium phosphate ($\text{Ca}_3\text{P}_2\text{O}_8 + 4\text{H}_3\text{PO}_4 = 3\text{CaH}_2\text{P}_2\text{O}_7$) and I have seen the statement, over the name of a well-known chemist, that "free phosphoric acid and insoluble phosphates cannot exist together." As a matter of fact the above reaction, like many others, is seldom, and only under exceptional circumstances, complete, and free phosphoric acid and insoluble phosphates not only can, but almost invariably do co-exist in tartar substitutes. This fact has an important bearing on the analysis of these substances.

As examples of the composition of the two extreme types above described, the following analyses may be given:

| | Class I. | Class II. |
|---|--------------|--------------|
| Moisture | 4.41 | 2.42 |
| Monocalcium phosphate (crystallized)..... | 49.67 | 29.48 |
| Monomagnesium phosphate (crystallized)..... | 2.75 | 3.54 |
| Free phosphoric acid (hydrated)..... | 2.02 | 0.73 |
| Insoluble calcium phosphate..... | 13.08 | 8.66 |
| Calcium sulphate (anhydrous)..... | 0.85 | 48.70 |
| Silica, etc. | 0.3 | 0.13 |
| Starch..... | 26.00 | 3.27 |
| Alkaline salts, water of crystallization, and unde-
termined | 0.92 | 3.07 |
| | <hr/> 100.00 | <hr/> 100.00 |

100 lbs. will neutralize sodium bicarbonate..... 45 lbs. $\left\{ \begin{array}{l} \text{cold } 27\frac{1}{2} \\ \text{hot } 48\frac{1}{2} \end{array} \right.$

There are many grades in the market intermediate between these, prepared for special uses, but which may practically be regarded as mixtures of these two principal types.

EFFECT OF CHEMICAL COMPOSITION ON THE CHARACTER AND PRACTICAL BEHAVIOR OF THE GOODS.

Class I.—The acidity or neutralizing power of this class is entirely due to the monocalcium phosphate and the free phosphoric acid, the exact nature of the reaction with soda varying with the conditions of temperature, dilution, etc., etc., but mainly resulting in the production of dicalcium phosphate $\text{Ca}_2\text{H}_2\text{P}_2\text{O}_8$ and disodium hydrogen phosphate.

Both monocalcium phosphate and phosphoric acid being readily soluble substances, the reaction takes place practically to the same extent in hot or cold solution.

With goods of the second class, *i. e.*, containing calcium sulphate, the reaction with soda is quite different. The primary reaction of the monocalcium phosphate on the sodium bicarbonate is the same as in the foregoing, but on heating, a secondary reaction occurs between the calcium sulphate and the products of the primary reaction, probably thus: $3\text{Na}_2\text{HPO}_4 + 3\text{CaSO}_4 = \text{Ca}_3\text{P}_2\text{O}_8 + 3\text{Na}_2\text{SO}_4 + \text{H}_2\text{PO}_4$, which it will be seen, is equivalent to liberating a fresh quantity of acid. In other words, the presence of calcium sulphate compels the phosphoric

acid to do more work, and the final product is tricalcium instead of dicalcium phosphate.

This secondary reaction only takes place on heating, and is the more complete the longer the mixture is boiled. The practical effect of this in the use of tartar substitutes is of very great importance.

Goods of class I, whose neutralizing power depends entirely on their contents of monocalcium phosphate and free phosphoric acid, when mixed with sodium bicarbonate and water, liberate the carbonic acid gas at once and completely in the cold; and hence, if this combination is used in baking, it is necessary that the dough should be placed in the oven immediately after mixing, as otherwise the gas escapes and the resulting loaf is "heavy."

With goods of class II, on first mixing the dough a portion only of the gas is liberated (corresponding to the primary reaction), making the dough spongy, but on putting in the oven, the secondary reaction commences and a steady evolution of gas occurs, which keeps the loaf porous and light.

This two-fold reaction has, in fact, the same practical effect as is obtained by the use of a less readily soluble salt than monocalcium phosphate; *viz.*, the action is slower.

The special suitability of cream of tartar for baking powder purposes rests on its property of being only sparingly soluble in cold water, but quite readily so in hot water, the effect of which is that the carbon dioxide is developed in the right amounts at the right time; exactly the same result is obtained in tartar substitutes by means of the secondary reaction with calcium sulphate.

The calcium sulphate in some tartar substitutes cannot, therefore, be regarded as an adulterant, neither is it the result of carelessness on the part of the manufacturer; but it purposely forms part of the substance, and has an important, and for some uses, quite an essential function.

It is not my purpose at present to treat the matter from a hygienic point of view, but, inasmuch as calcium sulphate seems to be something of a bugbear to many health officers and state chemists, it may be pointed out that a greater part at any rate of this substance is actually converted in the baking process

into sodium sulphate, and further, that in the small amounts used in practical baking the resulting dose of the latter salt would be extremely small.

ANALYSIS OF TARTAR SUBSTITUTES AND STATEMENT OF RESULTS.

It might at first sight seem supererogatory to detail any methods of analysis of a material composed of such familiar substances as lime, phosphoric and sulphuric acids, magnesia, etc., etc., still more so to enter into a matter apparently so simple as the determination of the neutralizing power of an acid substance.

The determination of the working power of tartar substitutes, however, presents peculiar difficulties, so much so that an analyst inexperienced as regards these materials as a rule fails entirely to get results of any value whatever, and as regards the more complete analysis, the determinations of lime, phosphoric acid, etc., etc., indeed present no difficulty. But when the attempt is made to group the acids and bases, it frequently results in surprising misstatements.

A matter of primary importance in the analysis of tartar substitutes is the determination of the "strength," or neutralizing power, always stated in terms of sodium bicarbonate.

To determine this "strength," two obvious methods present themselves; *viz.*, titration with standard alkali, and the determination of the amount of carbon dioxide evolved from sodium bicarbonate by a known weight of the substance. Inasmuch, however, as the indications given by the above two processes are two entirely different things, it must first be decided before adopting one or the other method, exactly what is meant by "strength" in a powder of this kind.

When monocalcium phosphate and sodium bicarbonate are heated together in presence of water, the carbonate is decomposed until the salt Na_2HPO_4 is formed. This salt, although chemically "acid," is already strongly alkaline to phenolphthalein, the salt of the formula $\text{R}_2\text{H}_2\text{P}_2\text{O}_7$, probably being the neutral salt to this indicator. It is obvious, therefore, that "acidity" of tartar substitutes, as indicated by titration, is quite a different matter from their ultimate power of determining the liberation of carbon dioxide from carbonates.

Ordinarily, for reasons above given, the "evolution" method indicates a power of evolving carbonic acid gas very considerably in excess of the "acidity" as indicated by titration. Unfortunately, however, both methods offer ample opportunity for error.

When a mixture of acid phosphate and sodium bicarbonate is heated with water, the amount of carbon dioxide evolved is dependent on the relative proportions of the two substances, on time, temperature, dilution and a host of other factors; and, by varying the conditions, results can be obtained differing from each other and the truth, not slightly, but to an extent to render the test useless.

In an article on the "Commercial Valuation of Cream of Tartar Substitutes," *J. Anal. Chem.*, 4, 4, Prof. Chas. A. Catlin sums up the foregoing in the words "there is found to be no definite ratio between the neutralizing capacity of these preparations and their gas-evolving power when in admixture with alkaline bicarbonate under the conditions of the baking process," and advocates the use of a modified form of the evolution method on the ground that inasmuch as the use of these powders is to evolve carbonic acid gas from alkaline bicarbonate, their power of doing this under the conditions of the baking process is the sole criterion of value.

There is, however, another factor that must be considered; *viz.*, the reaction of the residue. It is no less necessary that a baking powder shall have a neutral residue, than that it shall evolve carbonic acid gas, and there is this much in favor of the titration method, that if properly conducted it indicates exactly the amount of sodium bicarbonate that can be used with a given sample of tartar substitutes to give a neutral residue.

I can quite endorse Prof. Catlin's statement, that the ordinary method of titration with alkali, either direct or indirect, fails to give the proper data, but if the titration is conducted with special precautions, adapting it to the case, it is in my opinion the most satisfactory method of determining the "strength" of tartar substitutes.

The method of valuation proposed by Prof. Catlin is a combination of the titration and evolution methods; *viz.*, first find-

ing by titration with alkali and phenolphthalein the neutralizing power of the sample, and then weighing up exactly the amount of chemically pure bicarbonate, introducing into the evolution apparatus together with its equivalent of tartar substitutes, and weighing the carbon dioxide evolved under certain specified conditions.

It would seem that the evolution part of this method is entirely dependent on the titration, for certainly, if, in the evolution experiment only the exact equivalent of sodium bicarbonate as found by titration is used, the carbon dioxide corresponding to this and no more can possibly be evolved, and inasmuch as under the conditions laid down by Prof. Catlin for the evolution experiment, nearly all tartar substitutes will evolve carbon dioxide from more bicarbonate than is indicated by a properly conducted titration, the evolution experiment can at best only confirm the titration, and had better be altogether dispensed with as a troublesome and useless adjunct.

Prof. Catlin's paper contains many extremely valuable data as to the actual conditions to which the leavening agents are exposed in the practical baking process, and as emphasizing the necessity of making analytical tests as nearly as possible under these conditions, is well worthy of attention.

The method of conducting the titration test differs with the character of the sample to be tested.

In the case of tartar substitutes of class I (*i. e.*, practically free from calcium sulphate) the amount of alkali neutralized is practically the same whether the titration be conducted hot or cold.

With class II, or intermediate grades containing any considerable amount of calcium sulphate, this is not the case, for when titrated in the cold, the solution reacts alkaline to phenolphthalein as soon as the primary reaction between soluble phosphoric acid and soda is complete. If now this solution be heated, the secondary reaction, previously explained, commences; the red color of the phenolphthalein gradually disappears, till on full boiling it will be found that a very considerable amount of alkali must be added before neutrality is restored. Hence, tartar substitute containing calcium sulphate shows one strength cold and a much greater strength hot; or, as it is expressed in trade, "sulphate of lime base goods show a *cold* test."

As before stated, in the case of goods free from calcium sulphate, the "hot" and "cold" tests are identical, or they "have no cold test."

It will be understood that the difference between the hot and cold test is purely a function of the secondary reaction with calcium sulphate, and from the relation between the two tests an expert can form a tolerably close estimate of the amount of this substance present.

To return to the titration, the test is best made on one gram of the substance suspended in about thirty cc. water in a porcelain basin, and titrating with caustic alkali (carefully freed from carbon dioxide), using phenolphthalein as indicator. The one essential of the method is to use a very large amount of the indicator. If the titration is made using only one or two drops of phenolphthalein, as would ordinarily suffice for an acidimetric titration, a far larger amount of alkali can be added, before the faintest pink color is obtained, than is really required. This may be readily shown by adding a further considerable amount of phenolphthalein when the faint pink darkens to deep red, and on titrating back with acid a considerable amount must be used before the color disappears. For this reason an inexperienced operator always obtains results far too high.

The most convenient method of procedure when working with unknown samples is, first to make a cold titration, adding a large amount of phenolphthalein and titrating to a faint pink. The alkali should be added drop by drop with constant and vigorous stirring to break up the little clots of precipitated phosphates formed by each drop.

In the case of sulphated goods the first pink tinge indicates the "cold test" and the burette reading should be recorded. The solution is then rapidly brought to a boil under the burette, and if the pink disappears more alkali is added till the very faintest color reappears.

This first test serves as a guide for a more exact titration in which it is best to add nearly the full amount of alkali required, drop by drop as before, then bring to a brisk boil, add the phenolphthalein and finish the titration rapidly while still actively boiling. The ending should be the first faint pink permanent

for one minute at a boiling temperature. The end reaction is not sharp and is very difficult to determine exactly.

With heavily sulphated goods prolonged boiling will cause the pink to disappear owing to the greater completeness of the secondary reaction; but as Prof. Catlin has pointed out, in the baking process the chemicals are exposed to a temperature of 100° for a period not exceeding one minute at the most, and therefore in the test this time of boiling should not be exceeded.

Any process of indirect titration, by adding alkali in excess and titrating back with acid is entirely inadmissible, as is also any separation of the insoluble portions of the powder by filtration before titrating.

The more complete analysis of a tartar substitute involves the determination of the phosphoric acid, and *the forms in which it exists*, the lime, magnesia, starch, sulphuric acid, and occasionally iron and alumina.

The determination of these substances requires no special notice, except as regards the forms in which the phosphoric acid exists, which is a matter of the highest importance in determining the relative merits of tartar substitutes.

Disregarding the small amounts combined with magnesia, iron, and alumina, the phosphoric acid in tartar substitutes is present in three different states:

“Free,” or uncombined.

Combined with one molecule of lime, as $\text{CaH}_2\text{P}_2\text{O}_7$.

Combined with more than one molecule of lime as insoluble phosphates; and in order to make an analysis of any value whatever, it is absolutely necessary to determine the amount present in each of these forms.

The “free” acid may be determined by titration with standard alkali and methyl orange, which indicator reacts neutral with salts of the formula $\text{R}'\text{H}_2\text{PO}_4$, and consequently indicates the “free” phosphoric acid only.

The titration is best effected on the filtered aqueous solution, adding standard alkali to pink-yellow color. Inasmuch as a slight precipitate forms before the point is reached the indications are a trifle too high, but sufficiently accurate for all technical purposes.

For the determination of the phosphoric acid existing as monocalcium phosphate and insoluble phosphates two analyses are necessary.

First, the *total* phosphoric acid on the solution of the powder in acid, and secondly, the "water soluble" phosphoric acid, best extracted by shaking a weighed quantity with water in a graduated flask, filtering clear and determining the dissolved phosphoric acid in an aliquot of the filtrate.

The phosphoric acid can of course be determined by any orthodox method, but for convenience and rapidity the volumetric method of Pemberton, (this JOURNAL, July, 1893) far surpasses any other.

The total phosphoric acid minus the "water soluble" gives the "insoluble" phosphoric acid, which may exist as $\text{Ca}_3\text{P}_2\text{O}_8$, $\text{Ca}_2\text{H}_2\text{P}_2\text{O}_8$, or frequently as a mixture of the two. The determination of the insoluble phosphoric acid by difference is far more satisfactory than a direct determination.

The "water soluble" minus the "free" equals phosphoric acid existing as $\text{CaH}_2\text{P}_2\text{O}_8$.

It is necessary here to call attention to a very vicious practice followed by some chemists. Instead of determining the three forms of phosphoric acid as above, they determine only the *total* phosphoric acid and the total CaO. The CaO they then calculate into $\text{Ca}_3\text{P}_2\text{O}_8$, an excess of phosphoric acid of course remaining uncombined—which excess they then combine with the $\text{Ca}_3\text{P}_2\text{O}_8$, according to the reaction $\text{Ca}_3\text{P}_2\text{O}_8 + 4\text{H}_2\text{PO}_4 = 3\text{CaH}_2\text{P}_2\text{O}_8$, leaving an excess of either $\text{Ca}_3\text{P}_2\text{O}_8$ or H_2PO_4 as the case may be, but necessarily showing only one or the other.

Such a calculation cannot by any chance give correctly the composition of the substance for the reason before gone into, that tartar substitutes always contain both free acid and insoluble phosphates.

One word as to the form of stating results may not be out of place as this is a frequent source of *apparent* disagreement between two analyses that are really identical—a matter that it is often difficult to satisfactorily explain to the lay mind.

Having found, correctly or otherwise, the amount of monocalcium phosphate present in a sample, the analyst generally

states this in his report in the anhydrous form, $\text{CaH}_4\text{P}_2\text{O}_8$, calling it variously "monocalcium phosphate," "acid phosphate of lime," and occasionally "superphosphate," or some other name.

Equally in the case of calcium sulphate, it is a usual practice to report in the anhydrous form CaSO_4 , and to call it variously "sulphate of lime," "gypsum," "terra alba," "plaster of Paris," etc., etc., according to the state of mind of the analyst. Even the starch present in tartar substitute is capable of being reported under the misleading term of "organic matter."

Having reported the salts as present in their anhydrous state, the difference between the sum of results and 100 is put down as "combined water," etc., etc.

While such a method of reporting is very convenient, as saving trouble of calculation and giving a pretty analysis adding up exactly to 100.00, it is doubtful if it is the best way.

In my opinion the results of an analysis should always be reported in a form as nearly approaching the truth as may be, and at any rate the statement should always show on the face of it exactly what is meant.

In the case in point, monocalcium phosphate always exists (and indeed can only exist) in a crystallized state, and in consequence it would seem to better represent the truth if stated in this form and called "crystallized monocalcium" or "acid phosphate."

With regard to the calcium sulphate in highly sulphated goods, it appears to exist partly in the anhydrous state and partly crystallized, and as it is impossible to determine the amount of water of crystallization, the exact statement of this cannot be made. It is, however, easy to convey exactly what is meant by stating either as "anhydrous" or "crystallized" calcium sulphate.

The practice of calling calcium sulphate found by analysis "terra alba," "gypsum," etc., etc., is to be unqualifiedly condemned, as it suggests, and is intended to suggest by implication, a fraudulent addition of a foreign substance,—a suggestion that is justified neither by the analytical data nor the real facts of the case.

The neutralizing strength should always be stated in terms of

sodium bicarbonate neutralized by 100 parts of the sample, and where there is a considerable difference between the hot and cold tests, this should be stated, as it is an important factor in deciding as to the suitability of a tartar substitute for any particular use.

The best grades in the market have a neutralizing strength of 100 parts equivalent to forty-four to forty-five sodium bicarbonate, *i. e.*, about the working strength of cream of tartar.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE, No. 3.]

THE ANALYSIS OF VARNISHES.

BY PARKER C. MCILHINEY, PH.B., A.M.

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At present varnishes are seldom analyzed because no means are known of determining with any approach to accuracy, the amounts of the substances composing them. The tests used are practical ones and usually consist in varnishing a suitable surface with the sample to be tested and subjecting the varnished object to treatment as nearly as possible like that which it will receive in practice. If it is desired to ascertain the proportions of the different constituents, practical varnish-makers claim to be able to make up samples which will match in properties one to be tested, and in this way to arrive at the proper result. However this may be, it is out of the question for the chemist who is not a varnish-maker to use such a process. If methods can be devised whereby a chemist can make an actual analysis with a fair degree of accuracy, buyers can be certain of what they purchase and manufacturers can work more intelligently.

The different kinds of varnish may be classified as follows:

1. Spirit varnishes.
2. Volatile oil varnishes.
3. Fixed oil varnishes.
4. Miscellaneous; collodion varnishes, etc.

Spirit varnishes are composed of a resin dissolved in alcohol. Shellac spirits, made by dissolving shellac in wood or grain alcohol, is the most common.

Volatile oil varnishes are made by dissolving a resin in turpentine. Dammar varnish is a good example. Benzine is largely used as a substitute for turpentine in this and other varnishes.

The most important class is the fixed oil varnishes, and it is the analysis of this sort which will be considered. They are made from linseed-oil, a resin, and turpentine.

The principal resins used are kauri, manilla, and hard copals, such as Zanzibar. Common rosin is largely used as an adulterant. Kauri is the resin used by far the most, and there are many grades, varying in price from three cents to sixty cents a pound. Manilla stands next in the amount used, and of the others comparatively small quantities are used.

The resins used in fixed oil varnishes are in their natural state insoluble in linseed-oil and in turpentine. It is only after undergoing a process of roasting or distillation that they become soluble, and in this operation they lose from twenty to twenty-five per cent. in weight. In the process of manufacture the resin is first melted down in a kettle, and after it has been sufficiently heated the proper quantity of linseed-oil, also hot, is added, and the mixture heated some time longer to effect a combination between the oil and resin. After cooling somewhat, sufficient turpentine is added to properly thin the varnish.

It is difficult for several reasons to obtain samples of varnish for experiment in which the proportion of the constituents is known. They cannot be made successfully in small quantities as they are then of poor quality, and results obtained from such samples cannot be trusted. Through the kindness of Prof. A. H. Sabin, three samples of varnishes of known composition were obtained for experiment.

The Determination of Turpentine.—H. J. Phillips (*Chem. News*, **63**, 275, and *J. Soc. Chem. Ind.*, **10**, 577) proposes to distill off the turpentine at 220° C., using about 150 grams of varnish and catching the distillate in a tared flask. A current of coal-gas is passed through the liquid to prevent oxidation of the linseed-oil, and at the same time to assist in the removal of the turpentine vapor by carrying it away as fast as formed, and by agitating the liquid. The method is open to several objections; any vapors of naphtha in the coal-gas used are likely to be caught

and contaminate the turpentine. This difficulty would be overcome by the use of carbon dioxide instead of coal-gas, but carbon dioxide is not usually available in sufficient quantity. The author does not use any condenser, but depends upon the cooling of the neck of the retort used by the air, which is not sufficient. The residue left after most of the turpentine is gone is very viscous and retains some turpentine very persistently.

Mills (*J. Soc. Chem. Ind.*, 5, 222) says that the volatile constituents of varnish are easily determinable by evaporation with water.

Attempts were made to effect the removal of turpentine by distilling it off in a vacuum. Trials were first made using twenty-five grams of substance and a temperature of 100°–120° C., but this proved to be much too low a temperature and it was subsequently found that by using five grams instead of twenty-five grams of substance the results were better.

The method used was as follows: A portion of the varnish is weighed into a tared, round-bottom flask which is then heated in a paraffin bath at a temperature of 180° C. for four to eight hours, the air and vapor being removed from the interior of the flask by a pump. The flask is then again weighed and the loss in weight represents turpentine.

The results by this method were as follows:

| Varnish used. | Per cent. of turpentine found. | Per cent. present. | Quantity of substance used. |
|---------------|--------------------------------|--------------------|-----------------------------|
| A..... | 52.7 | 60.0 | 25 grams. |
| B..... | 34.9 | 41.4 | 25 " |
| C..... | 52.7 | 56.9 | 5 " |

The results are thus seen to be too low and irregular, and the residues smelled of turpentine. It was found that these traces of turpentine could be removed, and correct results obtained by adding to the contents of the flask after cooling two or three cc. of petroleum ether of very low boiling-point, allowing the residue to dissolve, and then carefully exhausting the flask of air, and finally heating gently. Of course, in these experiments it is necessary to use round-bottom flasks. The great objections to this method are that it does not distinguish between turpentine and any other volatile substance, and also that it requires arrangements for exhausting air, which are not always available. The

non-volatile residue is, however, in the very best condition for further examination.

Another method which has been used is a determination of the loss in weight on evaporating off the turpentine in the air-bath at 100° C. from a quantity of varnish contained in a watch-glass. This method is open to the same objections as the previous process, and the residue is not in good condition for further examination on account of the drying of linseed-oil. The fact that linseed-oil increases in weight on exposure to the air tends to give too low results. The formation of a film of dried varnish preventing further evaporation renders it necessary to use only small quantities of substance. In experimenting with the process it was found better to use watch-glasses of flat form than the ordinary concave ones. Three-quarters to one hour exposure at 100° and 0.400 to 0.500 gram substance gave the best results.

The following figures were obtained in this way:

| Varnish. | Amount found. | Amount present. |
|----------|---------------|-----------------|
| B..... | 40.8 | 41.4 |
| C..... | 56.0 | 56.9 |
| D | 53.4 | 56.8 |

The requirements of a satisfactory process for determining turpentine are:

- (1) That the volatile material shall be separated under conditions which admit of its being actually weighed or measured and then submitted to further treatment.
- (2) That the non-volatile portion shall be subjected to as little heat as possible, both to avoid any destructive distillation and to leave it unaltered for further examination.
- (3) The process should require no unusual apparatus. None of these processes fulfill the above conditions.

It is well known that on distilling together two immiscible liquids, such as carbon disulphide and water, the boiling-point of the mixture is lower than that of the more volatile liquid. Carbon disulphide boils at 49° , but when distilled with water the boiling-point of the mixture is 43° (Kundt, *Jahresb. Fort. Chem.*, 1870, 49).

On distilling together 100 cc. of water and five cc. of turpentine it was found that the first ninety-five cc. of distillate contained all the turpentine which separated very well from the

water. Experiment showed that ninety cc. of water either dissolve or hold in suspension permanently about 0.3000 gram of turpentine. On these principles the following process was devised:

Twenty-five grams of varnish are weighed into a flask of 400 cc. capacity, in which has been placed a piece of granulated tin, or its equivalent, to prevent bumping and about ten cc. of water. The flask is in this way prevented from becoming greasy, which would cause violent bumping. The contents of the flask are now submitted to distillation, the distillate being caught in a tapped separator. When ninety or ninety-five cc. of water have come over, the distillation is stopped and the turpentine and water allowed to separate. If the contents of the flask still retain any odor of turpentine more water should be added and the distillation resumed. After settling for a sufficient length of time, the water is carefully drawn off and the turpentine poured into a tared flask and weighed. A correction is made for the amount of turpentine retained by the water, amounting to 0.300 gram for ninety cc. of water. In some experiments salt was added to the water to raise its boiling-point, but no apparent advantage was gained except when the non-volatile residue was heavier than water; in this case the salt prevented the residue from sinking to the bottom and causing bumping by greasing the flask. If it is desired to examine the residue, the remaining water is poured off from it and alcohol added. On distilling off the alcohol, and if necessary removing the last of it by the addition of a little ether, which is also evaporated off, the residue is obtained pure.

The following results were obtained by this process:

| Varnish. | Per cent. found. | Per cent. present. |
|----------|------------------|--------------------|
| B..... | 41.2 | 41.4 |
| C..... | 57.1 | 56.9 |
| D | 56.3 | 56.8 |

The sample D was made by dissolving common rosin in turpentine, and it was therefore more difficult to remove the last trace of turpentine from the non-volatile residue than it ever is in an oil varnish, but even in this case the result is fairly accurate.

The method requires no unusual apparatus and can be carried out in about half an hour. The residue is not heated above the

boiling-point of water, and the turpentine is actually weighed and may be itself analyzed.

For the determination of benzine in turpentine, the method of Burton (*Am. Chem. J.*, **12**, 102) gives the best results. It depends upon the conversion of turpentine into acids soluble in water by the action of nitric acid while benzine remains unaffected and is separated and measured or weighed.

The Non-volatile Portion.—The analysis of the residue consisting of linseed-oil and resin, both more or less altered by heat, presents an extremely difficult problem in proximate analysis and one which yet remains unsolved.

The properties of resins have been investigated analytically by ; Hirschsohn, *Pharm. Ztschr. f. Russland*, 1875, 225, and 1877, 1; *Pharm. Jour.*, **7**, 369, and **8**, 389.

Schmidt and Erban, *Sitz. d. Wiener. Akad.*, **94**, 917, and *Ztschr. angew. Chem.*, 1889, 35.

Mills, *J. Soc. Chem. Ind.*, **5**, 222.

Mills and Muter, *J. Soc. Chem. Ind.*, **4**, 96.

Williams, *Chem. News*, **58**, 224.

These investigators have made upon various resins the same tests which have been used in the analysis of oils; *viz.*, the acid figure, the Koettstorfer figure, the iodine figure, the per cent. of bromine absorbed, and the solubility in ether, alcohol, etc. Their results are given in the following table:

| Resin. | Variety. | Acid figure. | Koettstorfer figure. | Hübl figure. | Per cent. bromine absorbed. | Observer. |
|--------------------|-------------------------|--------------|----------------------|--------------|-----------------------------|--------------------|
| Amber ... | | 15.4 | 86.8 | 62.1 | | Williams. |
| " ... | | | 160.7 | | 53.53 | Mills. |
| " ... | | | 145.0 | | | Schmidt and Erban. |
| " ... | | | 144.6 | | | " " " |
| " ... Melted | | 0.0 | 38.9 | 4.8 | | " " " |
| " ... " | | 0.0 | 33.9 | | | " " " |
| Animé.... | Rough Demarara..... | 26.6 | 73.6 | 127.88 | | Williams. |
| " | Fine Zanzibar | 18.2 | 73.6 | 135.25 | | " |
| " | Unknown | 25.2 | 87.5 | 137.54 | | |
| " | | | 95.4 | | 60.22 | Mills. |
| Copal | Soft manilla | 131.6 | 184.1 | 137.79 | | Williams. |
| " | Borneo manilla | 141.4 | 176.7 | 138.04 | | " |
| " | Singapore manilla | 128.8 | 194.1 | 123.31 | | " |
| " | Cleaned Sierra Leone .. | 84.0 | 129.0 | 138.04 | | " |
| " | Rough Sierra Leone.... | 72.8 | 138.5 | 133.35 | | " |
| " | Rough Accra | 46.2 | 131.6 | 121.66 | | " |
| " | Rough White Cengola.. | 57.4 | 133.0 | 129.66 | | " |
| " | Fine Clean Red Cengola | 60.2 | 136.2 | 136.90 | | " |

| Resin. | Variety. | Acid figure. | Koettstorfer figure. | Hübl figure. | Per cent. bromine absorbed. | Observer. |
|-----------------------|--|--------------|----------------------|--------------|-----------------------------|--------------------|
| Copal | Unknown | 57.4 | 122.2 | 142.24 | | Williams. |
| " | " | | 123.9 | | 83.93 | Mills. |
| " | Reduced to $\frac{2}{3}$ by boiling, | | 128.9 | | 84.52 | " |
| " | Boiled | 114.4 | | | | " |
| " | Zanzibar | | 92.4 | | | Schmidt and Erban. |
| " | " | | 89.6 | | | " " " |
| " | " melted | 0.0 | 36.8 | | | " " " |
| " | " | 0.0 | 34.6 | | | " " " |
| " | White Angola | | 132.2 | | | " " " |
| " | " | | 129.7 | | | " " " |
| " | " melted .. | 93.6 | 118.8 | 44.9 | | " " " |
| " | " .. | 93.4 | 117.8 | | | " " " |
| " | Red Angola..... | | 148.0 | | | " " " |
| " | " | | 146.4 | | | " " " |
| " | " melted | 30.5 | 110.7 | 34.8 | | " " " |
| " | " | 30.0 | 109.8 | | | " " " |
| Dammar, Batavia | | 22.4 | 36.4 | 117.67 | | Williams. |
| " | Unknown | 26.6 | 31.1 | 142.24 | | " |
| " | " | | 52.3 | | 117.94 | Mills. |
| " | " | 33.0 | 47.1 | 63.6 | | Schmidt and Erban. |
| " | " | 30.6 | 46.5 | 63.5 | | " " " |
| Elemi | | 15.7 | 28.6 | 175.39 | | Williams. |
| " | | | 32.9 | | 122.23 | Mills. |
| " | | 22.3 | 25.1 | 85.1 | | Schmidt and Erban. |
| " | | 22.0 | 24.0 | 80.9 | | " " " |
| Kauri | Medium..... | 63.0 | 99.3 | 151.13 | | Williams. |
| " | Fine | 51.8 | 77.4 | 164.21 | | " |
| " | " | | 128.8 | | 108.22 | Mills. |
| Rosin..... | Refined | 179.2 | 187.4 | 115.31 | | Williams. |
| " | " | 177.8 | 195.7 | 114.80 | | " |
| " | Ordinary..... | 169.4 | 176.4 | 112.02 | | " |
| " | " | 166.6 | 190.1 | 132.28 | | " |
| " | Refined | | 181.0 | | 112.7 | Mills. |
| " | Average of 5 samples .. | | | 155.5 | | McIlhiney. |
| " | Window glass | 159.1 | 170.4 | | | " |
| " | E. | 168.5 | 189.9 | | | " |
| " | A. Black..... | 155.7 | 195.1 | | | " |
| " | " | 146.5 | 168.2 | 116.8 | | Schmidt and Erban. |
| " | " | 145.5 | 166.0 | 114.6 | | " " " |

The corresponding figures for linseed-oil are as follows:

Acidity should be 0.0. Mills allows one per cent. KOH for acidity.

Koettstorfer figure (Allen, *Commercial Organic Analysis*, 2, 42). Nine samples, 187.4-195.2.

Hübl figure (Allen, *loc. cit.*, 50). Raw oil, 155-160; boiled oil, 148. Holde, *Mittheil. K. tech. Vers. Berlin*, 1891, 9, 81, and *J. Soc. Chem. Ind.*, 12, 179-180, 954.

Bromine absorption (Levallois, *J. pharm. chim.*, 1887, 1, 334), 100 per cent.

Mills (*J. Soc. Chem. Ind.*, **2**, 436). Raw oil, 76.09 per cent.; boiled oil, 102.36 per cent.

McArthur (*J. Soc. Chem. Ind.*, **7**, 64). Raw oil, 65.0-65.3 per cent.; boiled oil, 63.2-66.3 per cent.

The differences in solubility between linseed-oil and melted resins are but slight and are of little value in effecting separations in varnish analysis.

The Hübl figure is evidently useless as a means of quantitative analysis for the figures of linseed-oil and kauri the most frequently occurring resin, are almost identical.

The difference between the Koettstorfer figure is only about seventy-five, and even supposing that the figures of both oil and resin are known accurately, which is not the case, it would be difficult to make the analysis so carefully that the percentages of oil and resin would be correct.

Mills states that the analysis may be made by determining the acidity to phenolphthalein, and this proved to be correct, provided the mixture is composed of common rosin and linseed-oil and is not heated long. An analysis of such a mixture gave correct results but on attempting to apply the process to properly made varnishes the process was unsuccessful. Ten grams of a sample of varnish, known to contain 14.36 per cent. of kauri-resin, were diluted with a mixture of absolute alcohol, ether, and petroleum ether to obtain a clear solution, and then titrated with a solution of caustic soda in alcohol using phenolphthalein as indicator. The acidity found in this way was equal to only 0.345 per cent. of potassium hydroxide; this would mean an acidity of 2.40 per cent. for the kauri present, whereas Mills found 11.44 per cent., and Williams 6.3 per cent. Mills' statement that "it is evident that boiled oil when heated with a resin makes no difference in the resin's acidity," is not sustained by the facts.

The amount of bromine absorbed, as determined by the methods of Allen, Mills, and Levallois, is of no more use than the Hübl figure. The results depend largely upon the conditions under which the analysis is conducted.

In view of the fact that the bromine-addition figure of rosin is 0.0, while that of linseed-oil is 102, it seemed very likely that by means of this figure it would be possible to analyze varnish

residues. To test the process, a mixture was made of fifty per cent. common rosin and fifty per cent. oleic acid. The bromine-addition figure of the oleic acid used was 51.78 per cent., and that of the mixture 25.7 per cent., corresponding to 49.6 per cent. of oleic acid instead of fifty per cent. In order, if possible, to obtain samples of boiled oil and kauri-resin in the same condition in which they are present in varnishes, a quantity of boiled oil was heated in a retort to a temperature of 290° C. and maintained at this temperature for one hour. A sample of clear kauri-resin was also heated in a retort until it had lost twenty-three per cent. of its weight. The non-volatile part of a varnish of known composition was analyzed at the same time. The figures obtained were as follows:

| Substance. | Bromine-addition figure. | Bromine-substitution figure. |
|--|--------------------------|------------------------------|
| Heated linseed-oil | 76.62 | 4.82 |
| Melted kauri-resin..... | 21.53 | 80.31 |
| Non-volatile of varnish C..... | } .. 89.16 | 22.84 |
| Kauri, 54.3 per cent., oil, 45.7 per cent. | | |
| Theoretical figures of above..... | 46.71 | 45.81 |

The process therefore fails to give any means of making this analysis on account of changes made by the process of manufacture in the properties of oil and resin. It is well known to varnish-makers that treating together, effects remarkable changes in their physical properties, and that a certain amount of heating is necessary to make them knit together and work properly in the finished varnish.

Gladding (*Am. Chem. J.*, 3, 416), has devised a process for determining common rosin in mixtures with fatty oils, depending upon the solubility of silver resinate in ether and the insolubility of silver oleate in the same medium. This process was tried on varnish but also failed to give satisfactory results. A varnish known to contain 14.36 per cent. of Kauri resin gave 25.9 per cent.

It is evident that the processes used in oil analysis are not adapted to the analysis of varnishes. The oil and resin react upon each other in some way not understood, giving rise to new compounds, and we must know something about what these compounds are, before the analytical problem can be solved.

THE ANALYSIS OF MALT.

BY JOHN A. MILLER, PH.D.

Received March 19, 1894.

HAVING been called upon during the past few years to assay a great many samples of malt I have been struck by the variation which existed between the results of my own analyses and those made by other chemists upon the same samples. The variations in some cases were too large to be placed within the possibility of experimental error. With the belief that these variations might, in part at least, be due to a greater or lesser degree of accuracy in the methods employed in the analysis of malt, I undertook a comparative investigation of three methods which are quite universally used.

From the stand-point of the brewer, the largest consumer of malt, what are the important points to be ascertained by the analysis of a malt sample?

1. Moisture.
2. Percentage of extract which the malt will yield when submitted to a miniature mashing process.
3. Diastatic power, that is the rapidity with which the starch contained in the malt is converted into sugar and dextrine.
4. The percentage of acidity (calculated as lactic acid) which the wort contains.

It has been claimed by some that the percentage of sugar formed and the amount of proteids dissolved is of importance in judging of the character of the malt. The amount of sugar is of no practical value to the brewer as the increase or decrease of the percentage of that article is entirely dependent upon the manner in which the malt is handled in the mash tub. The total nitrogen in the malt wort calculated as proteids is of little value since the percentage present in the finished beer will depend upon so many factors as to render the first results of comparatively little value. Amongst the factors which will influence this percentage are: Character of the water used in mashing; the use of a high or low initial mashing temperature; the length of time the wort is boiled in the kettle; the amount and character of the hops used; the character and quantity of yeast used; and the character of the fermentation.

The four points mentioned are of about equal importance in the assay of a malt sample.

The determination of moisture shows whether the malt has been properly dried and also whether the purchaser is not paying too high a price for an article which he can obtain very readily from the city water supply.

The determination of lactic acid is of value from the fact that it enables one to judge, within reasonable limits, of the age of the malt under examination. For example, a sample of malt which is low in moisture and high in lactic acid is an old malt which has been redried to bring down the high percentage of absorbed moisture.

In a first-class sample of malt the moisture should not run above five per cent., and the lactic acid 0.7 per cent.

Determination of Moisture.—Two methods were investigated in order to ascertain their relative accuracy. In the one method from two to four grams of ground malt was used; in the other twenty grams. In both cases the samples were heated to 100° C. until the weight was constant. Both methods gave results agreeing to within the third decimal place. The use of from two to four grams, however, is to be recommended:

1. Because it admits of the use of ground watch crystals for drying and weighing, thus preventing the absorption of moisture while the sample is cooling.
2. The time required to obtain a constant weight is much less than when twenty grams are used.

Determination of Extract.—The determination of the percentage of extract which a malt will yield is of very great importance, as upon this percentage, the value of the malt largely depends. It is evident that a sample of malt yielding fifty-five per cent. of extract has not the same commercial value as a malt yielding sixty per cent.

METHOD NO. I.

“Fifty grams of ground malt are weighed out as rapidly as possible (to avoid accession of water) and treated in a weighed beaker with 250 cc. of warm distilled water, of such a temperature that the initial heat of the mixture may be from 50°–52° C. The beaker containing the mash is placed in a water-bath and

the contents maintained at the same temperature for a quarter of an hour. The heat is then gradually raised till the immersed thermometer registers 59° – 60° C., and the temperature is then kept constant till a drop taken from the liquid ceases to give a blue color with iodine solution and nearly ceased to give a brown. This shows that all the starch and nearly all the erythrodextrine has suffered hydrolysis—a point which will be reached in about twenty minutes. The heat is then increased to about 70° C. in order to complete the saccharification, when the water in the bath is boiled for five minutes. This step which completes the process of mashing should be arrived at in about 100 minutes from the commencement of the operation. The beaker is then cooled and the contents filtered. The insoluble matter is washed with cold water and the filtrate is made up exactly to 400 cc. The density of the clear wort is next taken at 15.5° C. in the usual way by a specific gravity bottle. The excess of density over that of water (taken as 1,000) multiplied by 2.078 will give the percentage of dry extract yield by the malt. Instead of ascertaining the gravity of the infusion, the proportion of solid matter may be determined by evaporating a known measure of the wort to dryness in a flat-bottomed dish, so that the residue may form a thin film. The extract dried at 105° C. till constant in weight."

Two portions of fifty grams each of the same sample of malt treated as indicated above gave the following results:

| | I. | II. |
|----------------------------------|-----------------|-----------------|
| Specific gravity of the wort.... | 1.0284 | 1.0284 |
| Extract calculated by factor.... | 59.01 per cent. | 59.01 per cent. |

5.142 grams of the wort were then taken and placed in a wide flat-bottomed platinum dish and the extract dried at 105° C. to almost constant weight. The following was obtained:

| | I. | II. |
|-----------------------------|--------------|--------------|
| Weight of the extract | 0.3496 gram. | 0.3488 gram. |
| Average weight | 0.3492 gram. | |
| Percentage of extract..... | 55.87 | |

5.142 grams were again taken and placed in a flat-bottomed dish and this in a water oven, the temperature of which was kept at 70° – 75° C., and the extract dried to constant weight. The time required for this was about seventy hours.

| | I. | II. |
|-----------------------------|--------------|--------------|
| Weight of the extract | 0.3694 gram. | 0.3681 gram. |
| Average weight | 0.3687 gram. | |
| Percentage of extract..... | 58.992 | |

METHOD NO. II.

"Fifty grams of ground malt are carefully weighed as rapidly as possible. The ground malt is put into a copper beaker, the weight of which is known, and this beaker is placed in a water-bath. Water is now mixed with the malt to the amount of 200 cc.; at a temperature of 38° R. This temperature is held while the malt is continuously stirred for thirty minutes, when the temperature is raised to 58° R., 4° R. each five minutes. When the temperature of 58° R. is reached tests are made in order to find out whether the starch has been converted completely. Usually we find that after the temperature of 58° R. has been reached all the starch is converted. The mash is always held thirty minutes after the temperature of 58° R. has been reached, when it is boiled for five minutes, cooled off, and water enough is added to make the weight of the contents of the beaker, or the weight of the entire mash, 350 grams. The wort is then filtered off. After the wort has been filtered the specific gravity is taken from which the per cent. Balling is ascertained and the amount of extract in the malt computed to the following formula; *viz.*,"

$$\frac{(600 + \text{per cent. water}) \times \text{per cent. Balling}}{100 - \text{per cent. Balling.}}$$

Two mashes of fifty grams of malt gave the following:

| | I. | II. |
|------------------------------------|-----------------|--------|
| Specific gravity of the wort | 1.0385 | 1.0383 |
| Average specific gravity | 1.0384 | |
| Extract calculated by formula..... | 63.85 per cent. | |
| Moisture in the malt | 7.53 " " | |

5.192 grams of wort was then placed in a flat-bottomed dish and dried at 105° C. to almost constant weight. Results; *viz.*,

| | I. | II. |
|------------------------|-----------------|--------------|
| Weight of extract..... | 0.4520 gram. | 0.4522 gram. |
| Average weight | 0.4521 gram. | |
| Extract | 54.25 per cent. | |

The same amount of wort dried at 70°-75° C. for about seventy hours gave:

| | I. | II. |
|-------------------------|-----------------|--------|
| Weight of extract | 0.4924 | 0.4922 |
| Average weight | 0.4923 gram. | |
| Extract | 59.07 per cent. | |

METHOD NO. III.

Fifty grams of ground malt are weighed out as rapidly as possible, then placed in a weighed copper beaker and mixed with 200 cc. of water of a temperature of 40° C. The whole mixture is then carefully heated on an asbestos plate until the immersed thermometer registers 60° C. This temperature of 60° C. is maintained for twenty minutes, the mixture being almost constantly stirred during this time. At the end of twenty minutes a few drops of the solution are tested with iodine solution in order to ascertain whether the saccharification is complete. If the iodine gives the starch or erythrodextrine reaction the mash is further heated, the temperature being carefully raised 1° every two minutes until iodine solution ceases to give any reaction. It is very seldom that the temperature will go above 70° C. The flame is then removed, the mash cooled down and enough water added to make the total amount used equal to 400 grams, or the weight of the mash, that is, the malt plus the water equal 450 grams. After thoroughly mixing, the mash is thrown upon a plaited filter. The first half of the wort which filters through is thrown back upon the filter and then all which filters through collected. The specific gravity of this filtrate, or wort, is then taken by means of the Westphal balance. From this gravity the percentage given by Schultze's tables is ascertained and that number multiplied by 8.75, which gives the percentage of dry extract yield from the malt. The percentage can also be calculated by the use of the following formula:

$$\frac{(800 - \text{per cent. water}) \times \text{per cent. Schultze}}{100 - \text{per cent. Schultze.}}$$

The Schultze tables are so arranged that they give the amount of extract in 100 grams of wort of the specific gravity obtained. It would be a natural conclusion that the percentage represented by Schultze tables should be multiplied by 8 in order to obtain the amount of extract in 100 grams of malt, but this factor gives results which are below the absolute amount of extract which may be obtained from the malt. As the result of actual

brewing experience I am of the opinion that the percentage Schultze multiplied by the factor 8 represents the amount of extract which the average brewer obtains from his material in actual practice, although the absolute amount obtainable on a small scale is higher. Two mashes of fifty grams each gave:

| | I. | II. |
|--|-------------------|-------------------|
| Specific gravity of wort..... | 1.0285 | 1.0285 |
| Extract calculated from Schultze's
table. Factor 8..... | } 58.96 per cent. | } 58.96 per cent. |
| Factor 8.75..... | | |
| Extract calculated by formula | 64.487 " " | 64.487 " " |
| | 64.24 " " | 64.24 " " |

5.1425 grams of this wort were placed in a flat-bottomed dish and dried at 105° C. to almost constant weight. Results; *viz.*,

| | I. | II. |
|--------------------------------|--------------|--------------|
| Weight of extract..... | 0.3511 gram. | 0.3494 gram. |
| Average weight of extract..... | 0.3502 gram. | |
| Extract | 56.03 | per cent. |

The same amount dried at 70°-75° C. for about seventy hours to constant weight gave:

| | I. | II. |
|------------------------|--------------|--------------|
| Weight of extract..... | 0.3700 gram. | 0.3681 gram. |
| Average weight | 0.3690 gram. | |
| Extract | 59.04 | per cent. |

In order to ascertain what variation, if any, existed between these results and the absolute amount of extract obtainable I made another mash from the same sample of malt which had been used for the preceding experiments. Method No. III was used with this exception that it was not made up to 400 grams, but was at once thrown upon a filter and washed with water at a temperature of 58° C. until the filtrate gave no reaction for sugar with Fehling's solution. This filtrate was then made up to 1,000 cc. and an aliquot part dried at 70°-75° C. to constant weight. Two portions of ten cc. each gave:

| | I. | II. |
|--|--------------|--------------|
| Extract by weight in ten cc.... | 0.3237 gram. | 0.3236 gram. |
| " in 1,000 cc..... | 32.37 | 32.36 |
| Percentage of extract from malt, 64.74 | | 64.72 |
| Average percentage | | 64.73. |

The variations existing between the results obtained is apparent in the following table:

| | METHODS. | | |
|--|----------|---------|----------|
| | No. I. | No. II. | No. III. |
| Per cent. of extract calculated according to the directions of the method, 59.01 | | 63.85 | 64.487 |
| Method III using factor 8..... | | | 58.96 |
| " " " formula..... | | | 64.24 |
| Extract dried at 105° C. | 55.87 | 54.25 | 56.03 |
| " " " 70°-75° C. | 58.99 | 59.07 | 59.04 |
| Absolute per cent. of extract obtainable, | | | 64.73 |

A comparison of these results show that methods II and III give us figures agreeing closer to the actual amount of extract obtainable from the malt than method No. I, but even these are a little below the actual content. No. III, however, only slightly so. The results obtained by drying at 105° C. are too low and untrustworthy owing to a decomposition during the process of drying, as will be shown later in this paper. Looking at the results of the three methods as obtained by drying the extract at 70°-75° we find an excellent agreement between the maximum and minimum results, but a wide variation from the absolute amount of extract. This would indicate that a marked amount of starch was not saccharified and consequently would be lost as extract. It was only obtained by the washing of the grains with warm water.

Extract dried at 105° C.—In order to ascertain why the extract dried at 105° C. was so much lower than when calculated or dried at 70°-75°, a malt analysis was made with the following results:

| | Method III. | | |
|---|-------------|---|---|
| Calculated per cent. of extract using factor 8, 58.40 per cent. | | | |
| Extract dried at 70°-75° | 58.25 | " | " |
| " " " 105° | 54.01 | " | " |

The percentage of extract obtained by drying at 105° is over four per cent. lower than the percentage of extract obtained by the other methods. This would indicate that either the percentage of extract was actually lower than indicated by the other methods of determination, or that some substance had undergone decomposition and occasioned a loss which reduced the percentage. I was of the belief that the maltose had suffered decomposition at the temperature of 105° and therefore lowered the percentage of extract.

Determinations of sugar were consequently made:

1. In the wort obtained by method III and calculated to the total amount of extract obtained.

2. The maltose or sugar contained in the extract dried at 70°-75° was determined and a calculation made for the total from these results.

3. The sugar contained in the extract dried at 105° was determined and a similar calculation made.

| | Maltose. |
|--------------------------------|-----------------|
| Method No. III | 37.50 per cent. |
| Extract dried at 70°-75° | 37.50 " " |
| " " " 105° | 31.50 " " |

It will be seen that the percentage of maltose obtained from the extract dried at 105° is six per cent. lower than that obtained from the original wort and from the extract dried at 70°-75°. This rather clearly indicates that a decomposition of maltose has taken place with a consequent loss.

In every case the extract dried at 105° was almost black in appearance and had a distinct burnt sugar odor.

CONCLUSIONS.

1. Methods II and III give results almost equal in accuracy. No. III giving nearer the absolute amount of extract obtainable when the factor 8.75 is used. It is furthermore a preferable method as it requires less time for the analysis than No. II. And where a number of samples are handled, time is an important item.

2. Method I is inaccurate as the results obtained are much below the actual amount of extract.

3. The extract can not be determined by drying at 105° owing to the decomposition of the maltose at that temperature. This applies to the determination of extract in beer as well as in unfermented worts.

4. The washing of the grains until no sugar reaction is obtained and the subsequent drying of the extract at 70°-75° C. is impracticable, except for scientific purposes, as the amount of time required for the completion of an analysis is too great.

I would recommend method III as the simplest; it is accurate when the factor 8.75 is used, and requires the least time. It is the method upon which a subsequent paper on diastatic power will be based.

I wish, here, to express my sincere thanks to my assistant, Mr. W. I. Tibbals, for the very able and enthusiastic manner in which he has assisted me in this investigation.

NIAGARA UNIVERSITY, BUFFALO, N. Y.

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THE IODIDES OF NARCEINE.

BY G. B. FRANKFORTER.

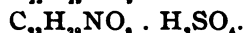
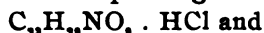
Received April 16, 1894.

THE alkaloid narceine when treated with iodine forms a characteristic blue substance analogous in many respects to the blue substance formed by the action of iodine on starch. This blue substance was first observed by Stein¹ in the early history of the alkaloid who regarded it as a periodide of narceine; but as pure narceine was then unknown, and as no definite formula was given for the substance, due allowance must be made in accepting his work.

The isolation of pure narceine and the determination of the new empirical formula, as well as the synthetic structure,² has made it necessary to repeat all of the early investigations. So far, at present, as this repetition has been carried out, different conclusions have been reached. This fact explains in a degree the variations and contradictions of the early investigators. The formula of narceine was finally fixed by Anderson³ as



and salts were prepared corresponding to



Later work on the alkaloids shows that both the chloride and sulphates are not salts of the base



but of a base containing one molecule of water less,



¹ *Fresenius' Zeitschrift für analytische Chemie*, 9, 390.

² Frankforter, "Beitrag zur Kenntniss des Narceins." Inaug. Dis., Berlin.

³ Anderson, *Liebig's Annalen d. Chemie. and Pharmacie.*, 86, 182.

In like manner the iodides of narceine were found to be derivatives, not of the Anderson formula, but the same less one molecule of water.

The Blue Iodide. $((C_{21}H_{27}NO_4)_2I_2 + 3H_2O)$ When narceine is treated with a water solution of iodine the blue iodide is formed, varying in color from a gray to an indigo blue, according to the amount of iodine used. By treating crystals of narceine direct with iodine, indigo-blue crystals are formed which still retain the same crystal form of narceine. By heating they change from long fine prismatic needles to short irregular ones. The blue crystals are slightly soluble in water, soluble with difficulty in alcohol, and quite insoluble in ether and chloroform.

On treating with dilute sodium hydroxide the blue color disappears, and when excess is avoided fine felt-like crystals of narceine are formed. By treating the blue crystals suspended in water with silver nitrate in the presence of nitric acid, beautiful hexagonal columns are formed which are now in process of analysis. The blue crystals contain three molecules of water which may be removed at $100^\circ C$.

0.3836 gram of the iodide lost 0.0118 gram at 100° .

| Found, $3H_2O$. | Calculated for,
$(C_{21}H_{27}NO_4)_2I_2 + 3H_2O$. |
|------------------|--|
| 3.07 per cent. | 3.29 per cent. |

ANALYSES:

| | |
|------|---|
| I. | 0.2020 gram iodide gave 0.4050 gram CO_2 , 0.1107 gram H_2O . |
| II. | 0.2632 " " " 0.5294 " " 0.1424 " " |
| III. | 0.3109 " " " 0.0912 " AgI. |

| | I. | Found,
II. | III. | Calculated for,
$(C_{21}H_{27}NO_4)_2I_2$. |
|---|-----------------|-----------------|-----------------|--|
| C | 54.65 per cent. | 54.82 per cent. | | 54.63 per cent. |
| H | 6.08 " " | 6.00 " " | | 5.10 " " |
| I | | | 15.95 per cent. | 16.01 " " |

Dried at 120° – 130° the blue color changes to a brownish, but changes back to the blue on cooling. The dried substance melts at 176° – $177^\circ C$. If heated rapidly a melting point of 180° – 181° may be obtained.

The Red Iodide. $(C_{21}H_{27}NO_4)_2I_2$. It was found that by treating narceine with an alcoholic solution of iodine a grayish-blue substance was formed which proved to have different properties

from the blue iodide. On standing in the air, or by gently heating, it changes to a red color and loses its well-defined crystal form. Dried at 110° – 120° it becomes brick red and changes slightly to the blue on standing some days in the air. It melts at 181° and is insoluble in water, alcohol, and ether. It contains three molecules of water which may be removed by drying at 90° – 100° .

0.2209 gram iodide dried at 100° – 110° lost 0.0092 H_2O .

| | |
|--------------------------------|---|
| Found, $3\text{H}_2\text{O}$. | Calculated for,
$(\text{C}_{21}\text{H}_{27}\text{NO}_8)_3 \cdot \text{I} + 3\text{H}_2\text{O}$. |
| 4.12 per cent. | 3.56 per cent. |

Analyses gave numbers which correspond best to the above formula.

ANALYSES:

- I. 0.1826 gram iodide gave 0.3770 gram CO_2 , 0.1025 gram H_2O .
 II. 0.3763 " " " 0.0546 " AgI.

| Found, | | Calculated for,
$(\text{C}_{21}\text{H}_{27}\text{NO}_8)_3 \cdot \text{I}$. |
|-------------------|----------------|---|
| I | II | |
| C 56.35 per cent. | | 56.63 per cent. |
| H 6.23 " " | | 5.54 " " |
| I | 7.84 per cent. | 8.00 " " |

Like the blue iodide it is transformed into narceine by carefully neutralizing with sodium hydroxide. In the presence of an alkali no iodide is formed. By treating with silver nitrate, slightly acidulated with nitric acid, fine long hexagonal columns crystallize out, on standing some hours in a cool place. The crystals are soluble in water and alcohol and melt at 110° – 112° . They are in process of analysis. It will be observed that the analyses give the per cent. of hydrogen too high. This was also observed in a great many analyses made in determining the new formula for narceine. In all these analyses, some of which were made by professional analysts, the hydrogen ran too high. So that it is barely possible that the formula for narceine may be changed from $\text{C}_{21}\text{H}_{27}\text{NO}_8$ to $\text{C}_{21}\text{H}_{28}\text{NO}_8$. This would raise the per cent. of hydrogen to 6.24, while the average of ten analyses made by four analysts gave an average of 6.4 per cent. This work was begun in the University of Nebraska, and for many favors received there, I wish to thank Prof. H. H. Nicholson.

UNIVERSITY OF MINNESOTA.

SOME SOURCES OF ERROR IN OUR METHODS OF DETERMINING POTASH IN FERTILIZERS AND GERMAN POTASH SALTS.¹

BY N. ROBINSON, REPORTER ON POTASH FOR THE N. A. O. A. C. FOR 1893.

IN common with many others, the writer has for some time entertained the belief that none of our recognized or official methods for determining potash in fertilizers and potash salts were above criticism. The objections to our American official methods from German and other sources are entitled to the highest respect, and per contra, the grave doubts expressed in high quarters among chemists in this country, as to the validity of the superior claims made for the Anhalt or Stassfurt methods, determined the writer for his own satisfaction to undertake a series of experiments, to ascertain, if possible, the sources of error, if any should be found to exist, in the three best known and most widely used ways of potash determination; *viz.*, the official or Lindo-Gladding, the alternate, and the Stassfurt or Anhalt methods.

This series of experiments was begun over two years since, and has been prosecuted as time permitted from that period to the present. The writer is constrained to admit that he had at the beginning a very inadequate conception of the difficulties to be encountered in the solution of the problem, or the wide scope of inquiry which anything like an exhaustive study of the questions involved.

The literature of the matter, while sufficiently voluminous on the general subject of potash determination, seemed to stop short at the very point where these inquiries must begin. Teschemacher and Smith, with the sanction of Fresenius and the apparent acquiescence of all the best German authorities, had declared that the removal of sulphuric acid was a *sine qua non* in all accurate potash estimations which, of course, at once excluded our chief American method from the list of "accurate" ones. Then came Zimmerman with a general and certainly rather formidable indictment of this same method. He charged that the

¹ Read before the World's Congress of Chemists, August 22, 1893.

ammonium-chloride solution was far from being a harmless and indifferent solvent of the miscellaneous impurities which are usually found in the potassium-platinochloride precipitate as obtained by the Lindo-Gladding method. Exact details were, however, wanting, or, at least not obtainable in any publication within the reach of the writer. Since then it is understood that one or two chemists in this country have undertaken investigations similar to those made by the writer, albeit the results of their work, perhaps from his somewhat isolated position, have failed to reach him.

It is with no little hesitancy, and he trusts with becoming modesty, that he is compelled to come into court with a general indictment against all our recognized or official methods of determining potash in fertilizers and potash salts. The writer does not make this sweeping charge lightly or without a full estimate of its gravity and of the overwhelming weight of authority which is likely at once to be marshalled against it. Methods of recognized value and almost universal acceptance are not dislodged without a struggle. The writer can only plead the evidence of the facts which he gives, and look patiently to the "calm judgment of the coming time" for the vindication of views which are presumably too radical for general acceptance, except as the result of extended and patient research at the hands of abler investigators than himself.

The First Count Against All Three Methods.—The first count in the indictment, and which is common to all our methods, comes from an obscure phenomenon, which so far as I am aware, has never been thoroughly investigated. For want of a better name I shall call it "The occlusion of potash salts by precipitates." Certain precipitates have long been known to manifest this peculiarity; but the bearing of this upon potash estimation seems somehow to have been overlooked. The fundamental fact is this. Many precipitates carry down potash salts and hold them so tenaciously that they cannot be washed out with hot water. All the precipitates thrown down in the customary working of our various official methods manifest more or less of this same tendency. Barium sulphate is probably the worst offender. Ferric and aluminic compounds are scarcely less chargeable with

this occult species of chemical larceny, while calcium, magnesium, and the other salts of the alkali metals are by no means free from suspicion of at least a mild form of the same tendency to hide and hold potash.

The Lindo-Gladding Method.—According to the investigations of Zimmerman and others—investigations which the tabular estimates by the writer given below, seem to fully confirm, in addition to the above source of loss coming from the “occlusion” of potash in “precipitates,” there are two other distinct and constant sources of error, with a number of casual and incidental ones, which may additionally vitiate results.

The first comes from the “alcohol washings” which, in the presence of the miscellaneous impurities nearly always found in the potassium platinochloride precipitate obtained by this method, result in the solution and consequent loss of the latter; and the second, from the fact that the solvent action of ammonium-chloride solution does not stop with the foreign salts which it is designed to remove; but that double decomposition often takes place. Potash is removed and ammonia substituted, involving the weighing of an impure potassium platinochloride, a portion of which is of different molecular weight. If we add to this the fact that calcium and magnesium sulphate, as well as ammonia, are not infrequently present in this same platinochloride, even when “washed to constant weight,” we are certainly entitled to suspect the absolute correctness of all potash estimates made by the Lindo-Gladding method.

Before giving tabulated results the writer may be pardoned for outlining in the briefest manner, the methods used in the work. In all cases, precipitates were washed with hot water until some time after any cloudiness was perceptible in the filtrate, either with barium chloride or silver nitrate. Potash was recovered from precipitates thrown down by ammonia and ammonium oxalate by re-solution and reprecipitation, and from barium sulphate by boiling the filter and its contents twice in dilute hydrochloric acid. The recovery of the potash from the ammonium-chloride washings seems to present the greatest practical difficulty. The ordinary method of volatilizing the ammonium salts over an open Bunsen flame involved so much loss of potash that no reliance

could be placed on the results. Fair work was done by exposing the well-dried material in a thin layer, in a shallow flat-bottomed platinum capsule on a portion of the sand-bath where the heat could be kept at the lowest vaporizing temperature of ammonium chloride, and consuming five or six hours in the operation. Another method involving several evaporations, incinerations, and filtrations with a slight loss of potash, was to add to the washings enough sulphuric acid to change all bases into sulphates, with appropriate subsequent treatment. The recovery of the potash from the "alcohol washings" seemed to present no special difficulty.

A word as to the factor of correction used for the potash already present in the ammonium-chloride solution. In my first experiments I assumed that the amount of potash present could be correctly estimated "by difference," by simply subtracting the weight of the undissolved portion from the five grams of potassium platinochloride first placed in the 500 cc. of the washing-fluid. The factor, 0.000195 per cc. thus obtained was used until recently without a suspicion of its inaccuracy. Some inexplicably discordant results led to a careful review of the whole matter. Analytical determinations showed that nearly twice as much potash was present in my ammonium-chloride solution as I had supposed. On carefully carrying out the official directions with another lot of this ammonium-chloride solution, I found that the potassium platinochloride had done something else besides "settle over night." Mutual decomposition had taken place. The ammonium-chloride solution was found to contain about as much potash in the form of chloride as platinochloride. The undissolved portion was a mixture of potassium platinochloride and ammonium platinochloride. The final amount as ascertained by several analytical determinations of the solution actually used, was potash corresponding to 0.00039 potassium platinochloride to the cubic centimeter, and the work as now given is corrected by that factor.

Still another factor of correction, small in all probability but still necessary for exact work, may be casually referred to. It is more than doubtful whether the potassium platinochloride precipitate obtained by the Lindo-Gladding method—in spite of all

its numerous "washings"—is ever strictly chemically pure. My observations indicate that, in addition to ammonium platinochloride, calcium and magnesium sulphate, and sometimes other impurities, are almost certain to be present. In the limited time at my disposal, I was unable to devise any satisfactory plan for the estimation of these impurities, and the tabulated results are, therefore, given without this correction.

In regard to the last example given (No. 6), which was from the "mixed potash sample" sent out to chemists in this country and Europe, it may be said that the quantity taken, $\frac{1}{4}$ gram, is too small for accurate work, as every error is, of course, quadrupled in the final result. These estimates were the last made, and lack of material prevented the employment of a larger quantity. As the results tally fairly well, however, with the work of others, they are given for what they are worth.

It will be observed that the "alternate" method is to a certain extent liable to the same objection as the Lindo-Gladding. Most of the loss here comes from the "occlusion" of potash in the barium sulphate. How seriously this affects the final estimate may be seen from the tabulated results given below.

A large amount of work done in the same line of investigation is omitted, but all leading substantially to the same results.

The six examples given are, indeed, selected from some twenty that were more or less fully carried out. Those taken are those in which the amount of loss by washings and precipitates is the lowest. In the course of the work some very anomalous results were obtained. In one case as high as thirty-four milligrams of potassium platinochloride were recovered from a barium sulphate precipitate weighing only 320 milligrams, and from which boiling water had ceased to dissolve out any more potash. Faulty manipulation may in some way have affected the result; but I think that any chemist who attempts to wade through the mass of work that I have gone over, and to unravel the singularly tangled skein of surface or molecular forces which govern the behavior of potash salts in the presence of barium sulphate and other precipitates, will meet with a good many surprises. He will find first of all, that the accredited statement of most chemical authorities that potash salts are not carried down by barium sulphate in acid

solutions, is altogether a fallacy. He will find that the amount carried down is subject to wide variations, and that, too, under conditions seemingly identical. He will probably come at last to the conclusion that this whole subject of the occlusion of potash salts by precipitates needs thorough and exhaustive investigation; and that until it is done and the losses resulting therefrom are eliminated, we must write "doubtful" after every potash determination made by processes involving this very obscure but very positive source of error.

ANALYSIS OF MIXED FERTILIZERS CONTAINING BONE, BLOOD, ETC.,
TOGETHER WITH THE SAMPLE OF MIXED POTASH SALTS SENT OUT BY
THE "REPORTER" BY THE LINDO-GLADDING METHOD WITH ESTI-
MATES OF LOSSES OF POTASH IN PRECIPITATES AND "WASHINGS."
MADE AT THE FLORIDA STATE LABORATORY, NORMAN ROBINSON,
ANALYST.

[illegible]

ANALYSIS OF SAME BY THE "ALTERNATE" METHOD WITH SIMILAR ESTIMATES OF LOSSES IN PRECIPITATES AND WASHINGS.

[illegible]

The Stassfurt or Anhalt Method.—As our German friends are naturally very partial to the Stassfurt method of determining potash in potash salts, the writer was led to make some tests to determine whether the same or similar objections could be urged against it as are believed to lie against our American methods. Concerning this plan of estimating potash, it may be said that it is not likely to be popular until one acquires considerable facility in its use. The accurate precipitation of the sulphuric acid is pretty certain to give trouble at first. If, however, the precipitation be made in a vigorously boiling solution, this difficulty vanishes. The barium sulphate is then heavy and crystalline, and settles like so much sand. After considerable experience in its use the writer has come to prefer this German method to any other from the fact that it involves less manipulation, gives an unusually clean precipitate of potassium platinochloride, and generally requires less alcohol for washing. The writer is convinced, however that it is chargeable with the same essential defect as the Lindo-Gladding and the alternate methods. It does not estimate all the potash present. The barium sulphate manifests the same peculiarity here as elsewhere.

From a previous dissolved sample of the mixed German potash salts sent out by the reporter, 200 cc. was taken, corresponding to five grams of material, precipitated as accurately as possible with barium chloride and made after cooling to 251.25 cc., and after vigorous shaking set aside for a few hours to secure the complete subsidence of the barium sulphate. (The volume of the latter was determined at 1.25 cc. by calculation from the barium chloride used and confirmed by subsequent weighing.) Ten cc. accurately measured of the clear solution corresponding to one-fifth gram gave 0.392 of potassium platinochloride $\times 5 = 1.960$ or 37.84 per cent., which closely approximate the average of the estimates made by German chemists; as much of the remaining liquid as could be moved without disturbing the precipitate was now poured off into a clean, dry beaker, and the precipitate with portions of this same solution was washed into an accurately calibrated fifty cc. measuring cylinder and again allowed to settle. After three hours the precipitate with the

mingled solution occupied a volume of sixteen cc. and did not seem inclined to go any lower. The clear liquid was now taken out with a pipette until exactly 21.25 cc. remained. The whole was now poured upon a dry nine cm. Schleicher and Schüll filter and exactly ten cc. filtered off and rejected. This of course left ten cc. of the solution and 1.25 cc. of the barium sulphate. The filter was repeatedly washed with hot water until no reaction was observable with silver nitrate. This last ten cc. of solution with the washings gave 0.4276 of potassium platinochloride or 22.6 mgms. more than the first ten cc. of solution examined, showing that this amount of potash was held up or occluded by the barium sulphate in a form that boiling water would remove. The filter with its precipitate was then boiled twice in twenty-five cc. dilute hydrochloric acid (one to five). In this way forty-four mgms. more potassium platinochloride were obtained. The total amount of potassium platinochloride recovered from the barium-sulphate precipitate was 66.6 mgms. or 0.01288 to each gram of substance = 0.247 per cent., or nearly one-fourth of one per cent. Other tests of the same material in smaller quantity gave considerably higher results, but as great care was taken to secure accuracy in every stage of the process, it is believed that the above fairly indicates the average loss where this particular material is estimated by the Stassfurt method. Much more extended investigations are required before any confident statements can be made as to the average loss from occluded potash when this method is employed.

Several other determinations exceeded this estimate. The instance given was carried out with special care. Full details of the methods used will be furnished to any one interested in the matter and perhaps not unfairly represents the average loss from this source.

In conclusion, it may be urged that, even conceding that there are some inherent defects in all our methods, since they are generally recognized and understood, and give fairly accurate results; anything looking towards a change is ill-timed and unwise. But what are we to consider "fairly accurate results?" As reporter on potash for the current year, the writer is compelled to echo an altogether too familiar refrain. We come up

here and, year after year, sing the same old tune. It is just as full of discord this year as it was last year and the year before that. To the question "How much potash?" working upon identically the same sample, New Hampshire says 12.13 per cent., New Jersey 12.76, New York and Maine 12.94, and North Carolina 13.08 per cent. and 13.22 per cent. Now here is a difference of considerably more than one per cent. in the same material, and that too, scattered along the whole gamut of rising estimates. Can these be considered "fairly accurate results?"

If we turn to our German friends, we find more unanimity but by no means complete agreement. Their answers to the same questions range from 13.10 per cent. to 13.44 per cent. Now who in this "confusion" of chemical tongues, has given us the right answer? Even on the face of it, is there not enough to suggest that there may be something wrong with the chemistry, as well as the chemists?

Notwithstanding the views and tabulated determinations above given, your reporter has no changes in existing methods to suggest. He only desires that the investigations he has outlined shall be submitted to careful re-examination, especially the "occlusion" of potash salts in precipitates, and that the relation of this as yet obscure phenomenon, to potash determination (a source of the error to which, so far as he is aware, the writer has now for the first time directed attention), should be made the subject of thorough investigation and review. If his conclusions are confirmed, changes are sure to come. Until then it seems the wiser course to adhere to existing methods.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 4.]

GANTTER'S PROCESS FOR DETERMINING THE IODINE FIGURE OF FATS.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received March 31, 1894.

F. Gantter, (*Ztschr. anal. Chem.*, **32**, 178 and 181) proposes a new method of determining the iodine figure of fats and oils in which he uses carbon tetrachloride as a solvent for both the fat and iodine and uses no mercuric chloride as, in the Hübl pro-

cess. He states that the figures obtained when mercuric chloride is used depend upon the amount used. The results which he obtained and from which he draws these conclusions are as follows:

| Substance. | Amount iodine used. | Amount HgCl ₂ used. | Iodine figure. |
|----------------------------|---------------------|--------------------------------|----------------|
| 0.100 gram linseed-oil.... | 0.100 gram. | 0.050 gram. | 83.5 |
| " " " " | 0.600 " | 0.000 " | 85.3 |
| " " " " | 0.150 " | 0.250 " | 141.0 |
| " " " " | 0.150 " | 0.500 " | 148.0 |
| " " " " | 0.600 " | 0.250 " | 156.4 |
| " " " " | 0.600 " | 0.500 " | 173.6 |
| " " " " | 0.600 " | 1.000 " | 188.4 |
| " " lard | 0.500 " | 0.000 " | 25.0 |
| " " " | 0.500 " | 0.250 " | 61.0 |
| " " " | 0.500 " | 0.500 " | 63.0 |
| " " " | 0.500 " | 1.000 " | 85.1 |

His results prove that the amount of mercuric chloride present influences the results and that a very large excess of Hübl's reagent would give a higher figure for linseed-oil than a moderate excess, but they certainly do not justify the conclusion which he draws from them that the use of mercuric chloride is unnecessary, and it is on this assumption that the accuracy of his process depends.

To ascertain whether fats would absorb from a solution of iodine alone in any suitable solvent as much iodine as would be necessary to convert them into saturated bodies, portions of a sample of oleic acid were treated with measured quantities of solutions of iodine in alcohol, carbon disulphide, and carbon tetrachloride. All these solvents dissolve both the oleic acid and iodine.

The results were as follows:

| Solvent. | Amount of oleic acid. | Excess of iodine in cc. N ₂ thio-sulphate. | Iodine figure. |
|-----------------------|-----------------------|---|----------------|
| Alcohol..... | 0.9947 gram. | 43.4 | 30.4 |
| " | 1.1445 grams. | 43.5 | 26.1 |
| Carbon disulphide ... | 0.9791 gram. | 58.9 | 52.7 |
| " " ... | 1.0044 grams. | 59.0 | 51.3 |
| Carbon tetrachloride. | 0.1171 gram. | 27.9 | 27.6 |
| " " | 0.1186 gram. | 28.2 | 24.1 |

The iodine figure of the sample as determined by the Hübl process was 80.0.

These results show that iodine alone will not saturate fats and if it is used for this purpose its action must be assisted by mercuric chloride. Gantter's process, therefore, does not determine the iodine figure but an arbitrary figure which is not comparable with the results obtained by any other process.

THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(Concluded from Page 332.)

BY THOMAS B. STILLMAN, PH.D.

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These results show that iodine alone will not saturate fats and if it is used for this purpose its action must be assisted by mercuric chloride. Gantter's process, therefore, does not determine the iodine figure but an arbitrary figure which is not comparable with the results obtained by any other process.

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STEVENS INSTITUTE OF TECHNOLOGY, DECEMBER, 1893.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 5.]

THE QUANTITATIVE SEPARATION OF ROSIN OIL FROM MINERAL OILS.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received March 31, 1894.

These two oils being both unsaponifiable are usually determined together as "unsaponifiable material" in the analysis of oils. They may be distinguished from one another by several methods.

1. *The Specific Gravity*.—Rosin oil has a much higher gravity than mineral oils, varying from 0.960 to 1.000 while heavy mineral oils range from 0.850 to 0.920.

2. *Valenta's Test*.—*Dingler's Poly. J.*, **252**, 297, and **253**, 418, *J. Chem. Soc.*, **48**, 93. Glacial acetic acid dissolves 2.67–6.50 per cent. by weight of mineral oil while rosin oil is soluble to the extent of 16.87 per cent. Mixtures, however, do not dissolve in proportion to the amount of rosin oil present.

3. *The Stannic Bromide Test*.—Allen, *Comm. Org. Anal.*, **2**, 463. A solution of stannic bromide in carbon disulphide gives, with small quantities of rosin oil in carbon disulphide solution, a purple coloration, while mineral oils do not.

4. *Solubility in Acetone*.—Demske and Morawski, *Dingler's Poly. J.*, **258**, 39. Acetone is miscible with rosin oil in all proportions while mineral oils require several volumes for solution.

5. *The Elaidin Test*.—Hager, *Ztschr. anal. Chem.*, **19**, 116. Rosin oil gives a dark red clear liquid while mineral oils remain unchanged.

6. *Ammonia Emulsion Test*.—Hager, *Muspratt's Tech. Chemie.*, 1893, **4**, 127, mixes two cc. of the oil to be tested with two cc. of petroleum benzine and four cc. of water and after shaking adds one cc. of ten per cent. ammonia; he then shakes violently and allows to stand for one to two hours. A persistent milky layer indicates rosin oil.

7. *Action of Sulphuric Acid*.—Hager, *Ztschr. anal. Chem.*, agitates a portion of the oil with an equal volume of concentrated sulphuric acid for five minutes and then pours into several volumes of cold water. Mineral oil gives a white milky liquid which separates into two clear light-colored layers. Rosin oil gives a gray or brownish milky liquid which separates an upper layer of yellow-brown color full of opaque flocks.

8. *The Color Produced with Sulphuric and Acetic Acids*.—Storch, *Analyst*, **13**, 71. Two cc. of the oil is shaken up with one cc. of anhydrous acetic acid and warmed gently. After cooling, the acetic liquid is removed with a pipette and a drop of strong sulphuric acid added which immediately produces a brilliant red color if any rosin oil is present. Cholesterin in many fatty oils gives a similar reaction. The same author determines rosin oil

quantitatively by its solubility in alcohol which is greater than that of mineral oils.

9. *The Hübl Figure*.—Valenta, *Dingler's Poly. J.*, **258**, 420. The Hübl figure of rosin oil is forty-three to forty-eight, while that of mineral oils is below fifteen.

10. *The Refractive Index*.—Holde, *Mittheil d. chem. tech. Vers. Anst.*, 1890, **8**, 269. With the Abbe refractometer the indices are as follows:

| | |
|-------------------|--------|
| Rosin oil..... | 1.5344 |
| Mineral oils..... | 1.4923 |

11. *Maumene's Test*.—*Muspratt Tech. Chem.*, 1893, **4**, 128. Rosin oil gives a rise of temperature of 42° C. Mineral oils only a slight rise. Allen, *Comm. Org. Anal.*, **2**, 462, says the rise in temperature of rosin oil is 18°–20° C.

12. *The Action of Nitric Acid*.—*Muspratt*, **4**, 127. Nitric acid of 1.185 sp. gr. when heated with rosin oil reacts violently with it giving off copious red fumes while mineral oils are but slightly effected.

Allen, *Comm. Org. Anal.*, **2**, 462, says that cold nitric acid is sometimes without immediate action on rosin oil but on warming a violent reaction often very suddenly ensues and after cooling, the rosin oil is found to have been converted into a more or less brittle red resin.

This process was investigated with a view to making it quantitative. Attempts were made to use nitric acid of 1.42 sp. gr. at a boiling temperature, but the frothing of the mass proved a serious difficulty, the liquid in every instance frothing out of the flask. Acid of 1.2 sp. gr. was found more manageable, the frothing in this case being slight. It was thought that the red resin might be dissolved in alkali, in which it appears to be quite soluble, and leave behind the mineral oil which could be dissolved in benzine, but this process could not be made to work satisfactorily. It was found, however, that the red resin produced from the rosin oil was insoluble in petroleum ether while mineral oil dissolves easily.

The process was therefore altered by diluting the products of the reaction with water and extracting with petroleum ether.

The following process gave satisfactory results:

Fifty cc. of nitric acid of 1.2 sp. gr. are heated to boiling in a flask of 700 cc. capacity. The source of heat is removed and five grams of the oil to be analyzed added. The flask is then heated on the water-bath, with frequent shaking, for fifteen to twenty minutes, and about 400 cc. of cold water added. After the liquid has become entirely cold, fifty cc. of petroleum ether are added and the flask agitated. The oil which remains unacted upon dissolves in the ether, while the resin remains in suspension. The liquid is poured into a tapped separator, leaving the lumps of solid resin as far as possible behind in the flask. After settling, the aqueous liquid is drawn off and the ethereal layer poured into a tared flask. Another portion of petroleum ether is added to the resin remaining in the flask and allowed to act upon it for about ten minutes, when it is added to that in the tared flask. After distilling off the ether the oil is weighed. Mineral oils lose about ten per cent. in this way, and hence the weight of oil found must be divided by 0.9 in order to find the amount present in the sample analyzed.

Allen found mineral oils to lose ten to twelve per cent. on treatment with nitric acid. *Pharm. Jour.*, [3], 11, 266.

A mixture of seventy-six per cent. of mineral oil with twenty-four per cent. of rosin oil gave, by this method, 76.8 per cent. of mineral oil.

RUTHENIUM AND ITS NITROSOCHLORIDES.¹

BY JAMES LEWIS HOWE.

A FEW years ago A. Joly² published the results of an investigation on the supposed tetrachloride of ruthenium of Claus, in which he showed that the double salts of this compound, the "red salt" of Claus, are in reality double salts of a nitrosochloride, RuCl_2NO . When his work came to my notice I was engaged in studying the compounds of ruthenium, especially seeking to discover a simple and certain way of forming the supposed tetrachloride. Being engaged at present on other compounds of ruthenium, I present in this paper results reached,

¹ Read before the Cincinnati Section, March 15, 1894.

² *Compt. rend.*, 107, 998; 108, 854.

chiefly respecting the nitrosochlorides. For the unexpected formula of these compounds I am indebted to Joly, as at the time of his publication I had not analyzed any of the compounds; the rest of the work was entirely independent of his researches, and in the cases where the same work has been carried out by each of us, his results are in every respect confirmed.

The crude ruthenium was purified by fusion with caustic potash and saltpeter, and distillation of the dissolved melt in a stream of chlorine, as RuO_4 . Good results were also obtained by treating the solution of the melt with potassium permanganate and sulphuric (or nitric) acid in the retort, and distilling. In either case the RuO_4 was received in dilute alcoholic potash. When the precipitate, or that obtained by treating a solution of the melt with nitric acid, is boiled for several days with aqua regia, in a flask provided with a return condenser, the ruthenium is completely converted into the nitrosochloride. (In his first paper Joly describes the formation of the nitrosochloride by treatment of RuCl_3 with a nitrite, and in his second paper by treatment with a large excess of nitric acid.) The solution in aqua regia is evaporated to dryness on a water-bath, the residue dissolved in water and treated with the chloride on an alkali; the corresponding double chloride then crystallizes out, either directly or on evaporation of the solution. The following salts have been studied, the analyses of the potassium and ammonium salts being given merely in confirmation of Joly's results.

1. *Potassium Ruthenium Nitrosochloride, or Potassium Nitrosochlorruthenate.* $2\text{KCl}, \text{RuCl}_3\text{NO}$, or $\text{K}_2\text{RuCl}_3\text{NO}$.—Formed by direct precipitation of very concentrated solutions of RuCl_3NO with KCl solution, or by evaporation of the mixed solutions. The analyses, as well as those of the other salts, were made by heating the salt in a stream of hydrogen and collecting the hydrochloric acid evolved in a solution of silver nitrate. The nitrogen of the NO group is reduced and deposited in the cooler portion of the combustion tube as ammonium chloride. Claus' analytical error, which led him to the formula $2\text{KCl}, \text{RuCl}_3$, was in not directly estimating the evolved chlorine, the loss Cl_3NO differing very slightly in weight from Cl_3 .

ANALYSIS.

| | Calculated. | Found. | |
|---------------------------------|-------------|--------|-------|
| | | I. | II. |
| Cl ₃ NO (loss)..... | 34.98 | 34.77 | 34.38 |
| Cl ₃ | 27.27 | 26.98 | 27.07 |
| NO (difference)..... | 7.71 | 7.79 | 7.30 |
| Ru | 26.77 | 26.65 | 25.99 |
| 2KCl | 38.24 | 38.41 | |
| Cl ₂ (in 2KCl) | 18.18 | | 18.62 |

SOLUBILITY.

At 25°..... 100 parts water dissolve 12 parts salt.

At 60°..... " " " " 80 " "

2. *Ammonium Ruthenium Nitroschloride.* 2NH₄Cl, RuCl₃NO.

—Formed as above from RuCl₃NO and NH₄Cl.

ANALYSIS.

| | Calculated. | Found. |
|-----------------------|-------------|--------|
| Cl ₃ | 50.96 | 50.34 |
| Ru | 30.02 | 29.61 |

SOLUBILITY.

At 25°..... 100 parts water dissolve 5 parts salt.

At 60°..... " " " " 22 " "

3. *Rubidium Ruthenium Nitroschloride.* 2RbCl, RuCl₃NO and 2RbCl, RuCl₃NO, 2H₂O.—When very concentrated solutions of RuCl₃NO and RbCl are mixed there is precipitated a small amount of rather pale-purple anhydrous salt. If solutions less concentrated are mixed and evaporated over sulphuric acid, the hydrated salt crystallizes out in large crystals, accompanied by some of the anhydrous salt. On evaporating a solution of the hydrated salt to dryness on the water-bath, or even on heating its solution, it is almost completely converted into the anhydrous salt.

a. *Anhydrous Salt.*—Fine pale-purple powder, which may be recrystallized from hot water in small, almost black crystals, closely resembling the potassium and ammonium salts, and which, like these, give a pale-purple powder in the mortar.

ANALYSIS.

| | Calculated. | Found. | |
|----------------------------------|-------------|-----------|-------|
| | | I. | II. |
| Cl ₃ NO (loss)..... | 28.27 | | 28.13 |
| Cl ₃ | 22.04 | | 21.89 |
| NO (difference)..... | 6.23 | | 6.24 |
| Ru | 21.64 | | 21.35 |
| 2RbCl (Rb = 85.2) .. | 50.09 | | 50.52 |
| Ratio Ru : 2RbCl.... | 1 : 2.314 | 1 : 2.294 | |
| Ratio Ru : Cl ₃ | 1 : 1.018 | 1 : 1.017 | |

(I was a mixture of anhydrous and hydrated salt.)

SOLUBILITY.

At 25°..... 100 parts water dissolve 0.57 parts salt.

At 60°..... " " " " 2.13 " "

b. Hydrated Salt.—Large dark-purple crystals, losing their water of crystallization very readily over sulphuric acid, and difficult to completely free from the adhering anhydrous salt.

ANALYSIS.

| # | Calculated. | Found. | |
|---|-------------|---|---------|
| | | I. | II. |
| Cl_3NO , $2\text{H}_2\text{O}$ (loss) | 33.26 | 31.70 | 32.43 |
| Cl_3 | 21.51 | 20.83 | 19.42 |
| NO (difference)..... | 5.79 | NO and
$2\text{H}_2\text{O}$ } 10.87 | NO 5.98 |
| Ru | 20.13 | | 19.75 |
| 2RbCl | 46.60 | 47. | |
| $2\text{H}_2\text{O}$ | 6.96 | | 7.03 |

(I had lost some water by standing over sulphuric acid before the first weighing was made.)

SOLUBILITY.

At 25°..... 100 parts water dissolve 114.3 parts salt.

4. *Cesium Ruthenium Nitrosochloride.* 2CsCl , RuCl_3NO and 2CsCl , RuCl_3NO , $2\text{H}_2\text{O}$.—As with the rubidium salts, when very concentrated solutions of RuCl_3NO and CsCl are mixed, cesium ruthenium nitrosochloride is partly precipitated as the anhydrous salt, while on evaporating the less concentrated cold mixed solutions over sulphuric acid, large crystals of the hydrated salt are formed. Some of the anhydrous salt is usually formed at the same time, even in the cold. On evaporating a solution of the very soluble hydrated salt on the water-bath to dryness, it is completely changed into the very slightly soluble anhydrous salt. I have not found it possible to form the hydrated salt from the anhydrous, nor to obtain the anhydrous salt in crystals large enough to be seen by the naked eye.

a. Anhydrous Salt.—Fine pale-purple powder, not differing in appearance from the rubidium salt, but less soluble.

ANALYSIS.

| | Calculated. | Found. | | |
|---|-------------|--------|-------|-------|
| | | I. | II. | III. |
| Cl_3NO (loss) | 23.61 | 23.85 | | 23.56 |
| Cl_3 | 18.41 | 17.93 | 18.19 | 18.41 |
| NO (difference) | 5.20 | 5.92 | | 5.15 |
| Ru | 18.08 | 17.62 | | 17.85 |
| 2CsCl ($\text{Cs} = 132.7$)..... | 58.31 | 58.40 | | 57.90 |

SOLUBILITY.

At 25° 100 parts water dissolve 0.20 parts salt.

At 60° " " " " 0.56 " "

b. Hydrated Salt.—Large dark-purple crystals, often ten millimeters long or broad. Loses water of crystallization readily over sulphuric acid.

ANALYSIS.

| | Calculated ₁ | Found. |
|--|-------------------------|--------|
| Cl ₃ NO, 2H ₂ O (loss) | 28.10 | 28.11 |
| Cl ₃ | 17.32 | 16.92 |
| NO (difference) | 4.90 | 5.59 |
| Ru | 17.01 | 16.63 |
| 2CsCl | 54.88 | 55.13 |
| 2H ₂ O | 5.87 | 5.60 |

SOLUBILITY.

At 25° 100 parts water dissolve 105.8 parts salt.

The properties of the nitrosochlorides agree almost, if not completely, with those ascribed to ruthenium tetrachloride by Claus¹ and M. C. Lea.² The most remarkable property, to which Joly has also called attention, is their stability.

Two and four-tenths grams of the potassium salt was heated with gradually increasing temperature in an air-bath. Up to above 250° the loss was less than 0.5 per cent. Direct heat was then applied to the crucible till the salt was partially decomposed, Cl and NO being evolved. The whole was then treated with water, and from the soluble portion the original undecomposed salt was crystallized. No trace of ruthenium trichloride was present, showing that the NO is not given off until the chlorine also passes off.

The solutions of the nitrosochlorides are unacted on by urea in acid or alkaline solutions, nor are they reduced by FeSO₄, Cu₂Cl₂, or SnCl₄. Hydrogen dioxide has no effect in acid solutions; in alkaline solutions oxygen is evolved, the solution becoming decolorized, but the change appears to be the same as that when the original solution is treated with excess of alkali.

Potassium permanganate has no reaction in acid solutions, but in alkaline solutions (with fixed alkalies) on boiling the green color of the manganate appears, soon followed by the

¹ *Bul. de l'Acad. Imp. de St. Pet.*, 1, 107; 4, 457.

² *Am. J. Sci.*, 38, 81, 248.

brown precipitate of the hydroxide, and the ruthenium salt is reduced to its trivalent condition. The solution after the reaction, gives the test for nitric acid, which is not the case with the original solution. It is then probable that the NO group is oxidized off by the permanganate.

Sodium hypobromite also reacts with the nitrosochloride in the cold, with evolution of gas; on acidifying with hydrochloric acid, RuO_3 is evolved with the bromine, a reaction analogous to the characteristic reaction of the trichloride with potassium chlorate and hydrochloric acid.

Potassium ferrocyanide gives no reaction in the cold with the nitrosochloride, but when *neutral* on boiling the solution becomes intensely deep brown, almost opaque unless very dilute. In acid solutions this reaction does not take place. Alkaline solutions become amber on boiling, but on careful neutralization with hydrochloric acid the brown coloration appears. An excess of acid changes the brown to a much less dense olive green, very different from the bright green produced by the trichloride with the ferrocyanide.

Sulphur dioxide has little effect in the cold, but when led into the warm alkaline solution of the nitrosochloride the solution gradually loses its rose color and becomes amber, and a precipitate is formed, very slightly soluble in water.

Potassium cyanide decolorizes the solution of the nitrosochloride on warming and a double salt seems gradually to be formed.

Oxalic acid has no apparent effect.

These last three reagents all have decided reactions with the trichloride and are now being further studied.

In the solutions of the heavy metals I have obtained no precipitates with the nitrosochloride, except with mercurous salts and those of silver. In both these cases a buff precipitate is thrown down, but on heating with nitric acid it is decomposed, the ruthenium passing into solution, the silver or mercurous chloride being left. Lead salts do not precipitate the nitrosochloride.

Copper sulphate gives no reaction, but on warming with excess of caustic alkali the copper hydroxide passes into solution, giving the azure-blue characteristic of Fehling's solution. From this, cuprous oxide is precipitated on warming with grape sugar.

When NO is led into a solution of ruthenium trichloride a change takes place, and the solution no longer gives the reactions for the trichloride; nor does it appear to contain the nitrosochloride. Differential characteristics for the nitrosochloride solutions as compared with the trichloride are the following:

Solutions rose becoming salmon pink on dilution.

No precipitate with excess of alkali.

No purple color on boiling with potassium thiocyanate.

No reaction with ammonia and sodium thiosulphate.

Deep brown on boiling with potassium ferrocyanide in neutral solution.

This last reaction is most characteristic.

Several attempts have been made by me to prepare a higher ruthenium chloride than the trichloride, but unsuccessfully.

RuO_4 dissolved in hydrochloric acid, yields on standing only RuCl_3 ; the same is true of RuO_4 dissolved in chlorine water.

RuS_2 was oxidized with HCl and KClO_4 ; much of the ruthenium was volatilized as RuO_4 , while the residue consisted solely of RuCl_3 .

In order to prove conclusively that the "red salt" of Claus was the nitrosochloride it was formed according to the method used by Claus; *viz.*, oxidation of RuS_2 with nitric acid.

ANALYSIS.

| | Calculated. | Found. |
|---------------------|-------------|--------|
| Cl_3 | 26.77 | 26.95 |

It seems at first sight entirely unexpected that we should find the group NO directly connected with a metal, but it is by no means unique. The affinity of ferrous salts for NO is familiar, and there are several comparatively stable compounds in which the group NO appears to be attached to iron, as the nitroso-pentasulphide and nitrosoheptasulphide, and the nitrosothio-carbonate. In the nitroprussides the NO group replaces in part the CN of the ferrocyanides. Iron and ruthenium occupy analogous positions in the periodic system, and as osmium is the third member of the series we should expect to find a similar and strong affinity of osmium for NO; indeed, Joly¹ has proposed to show that the osmiamic acid of Fritzsche and Struve has an

¹ *loc. cit.*

analogous constitution to the nitrosocompounds of ruthenium.

POLYTECHNIC SOCIETY, LOUISVILLE, KY.,

March, 1894.

ON THE CRYSTALLIZATION OF 2CsCl , RuCl_3NO , $2\text{H}_2\text{O}$ AND
 2RbCl , RuCl_3NO , $2\text{H}_2\text{O}$.

BY N. D. CLARK.

These salts are isomorphous and crystallize in the monoclinic system. They show a similar habit and the crystals of both salts that were submitted for examination measured as much as ten millimeters in length.

The forms which were identified are

| | | |
|------------------------|------------------------|-------------------------|
| a , 100, $i-\bar{i}$ | m , 110, I | e , 101, $-I-\bar{i}$ |
| c , 001, O | d , 021, $2-\bar{1}$ | o , 101, $I-\bar{i}$ |

The habit is prismatic like Figs. 1 and 2, while Fig. 3 represents a basal projection of Fig. 2. Of the forms in the prismatic zone m is always prominent while a is small and frequently fails. The prevailing forms that terminate the prisms are d and o , while c and e are usually either small or altogether wanting.

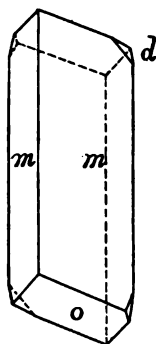


FIG. 1.

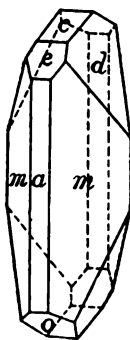


FIG. 2.

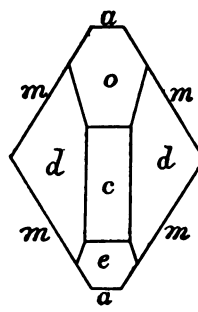


FIG. 3.

The axial ratios that are given beyond were calculated from the measurements that are marked by asterisks in the accompanying tables; the values cannot be regarded as very exact, as the crystal faces were slightly rounded and not adapted for accurate measurement. On the cesium salt the error in the fundamental measurements is regarded as not exceeding $\pm 8'$, while with the rubidium salt the error may exceed twice that amount.

| | | | | | |
|---|---|---|-----------------------|------------------------------------|-----------------------|
| | | $a : b : c$ | | | |
| $2\text{CsCl}, \text{RuCl}_3, \text{NO}, 2\text{H}_2\text{O}$ | | 1.698 | : 1 : 1.177 | $\beta = 76^\circ, 11'$ | |
| $2\text{RbCl}, \text{RuCl}_3, \text{NO}, 2\text{H}_2\text{O}$ | | 1.692 | : 1 : 1.242 | $\beta = 76^\circ, 50\frac{1}{2}'$ | |
| | Measured. | Calculated. | Measured. | Calculated. | |
| | $2\text{CsCl}, \text{RuCl}_3, \text{NO}, 2\text{H}_2\text{O}$ | $2\text{RbCl}, \text{RuCl}_3, \text{NO}, 2\text{H}_2\text{O}$ | | | |
| $a \wedge c$ | 100 \wedge 001 | $76^\circ, 11'$ | | $76^\circ, 50', 30''$ | |
| $c \wedge e$ | 001 \wedge 101 | $30^\circ, 0'$ | | $31^\circ, 18'$ | $31^\circ, 28', 28''$ |
| $d \wedge d$ | 021 \wedge 021 | $132^\circ, 45'$ | | $135^\circ, 4'$ | |
| $m \wedge m$ | 110 \wedge 110 | $62^\circ, 13'$ | $62^\circ, 27', 59''$ | $117^\circ, 30'$ | |
| $a \wedge m$ | 100 \wedge 110 | $58^\circ, 45'$ | $58^\circ, 46', 6''$ | $58^\circ, 50'$ | $58^\circ, 45'$ |
| $m \wedge d$ | 110 \wedge 021 | $33^\circ, 18', 30''$ | $33^\circ, 35'$ | | $33^\circ, 37', 33''$ |
| $c \wedge o$ | 001 \wedge 101 | $38^\circ, 34', 30''$ | $38^\circ, 53', 23''$ | $39^\circ, 32'$ | $40^\circ, 37', 9''$ |
| $a \wedge e$ | 100 \wedge 101 | $46^\circ, 12'$ | $46^\circ, 11'$ | $46^\circ, 6'$ | $45^\circ, 22', 2''$ |
| $d \wedge c$ | 021 \wedge 001 | $66^\circ, 22', 30''$ | $66^\circ, 30'$ | | $67^\circ, 32'$ |
| $a \wedge o$ | 101 \wedge 100 | $65^\circ, 13', 30''$ | $64^\circ, 55', 37''$ | $63^\circ, 33'$ | $62^\circ, 32', 21''$ |

Both salts show a perfect cleavage parallel to a and a poorer one parallel to c . The plane of the optical axes is the clinopinacoid; the double refraction is strong, and the optical orientation such that cleavage plates parallel to a show in convergent polarized light an optical axis almost in the center of the field.

This investigation was made in the mineralogical-petrographical laboratory of the Sheffield Scientific School, under the direction of Prof. S. L. Penfield, to whom the author's thanks are due.

AN IMPROVED MERCURY THERMOMETER FOR HIGH TEMPERATURES.¹

BY W. NIEHLS.

THE ordinary mercury thermometers give accurate values up to 250°C . When the thermometer tube above the mercury is filled with nitrogen under pressure, readings are possible up to 450°C .

Early in 1893 I submitted to the Physikalisch-Technische Reichsanstalt, at Charlottenburg, Berlin, which, as is well known, tests the correctness of normal thermometers, etc., models of high temperature thermometers which were capable of giving accurate readings up to 550°C . Since then minor details of construction have been satisfactorily completed, and in the following, I will briefly describe the perfected instrument.

¹ Read before the Cincinnati Section, April 16, 1894.

At the outset it was necessary to secure a variety of glass which does not soften below 600° . For this purpose the borosilicate glass of Jena was chosen and has shown itself well adapted in all cases. The graduation is brought directly on the tube, and ranges either from 180° to 550° in single degrees, or from 100° to 550° in intervals of five degrees. The scale is black, for the sake of the greatest clearness, and the method of its preparation is as follows: The thermometer tube is supplied with the requisite amount of mercury, and then completely filled with carbon dioxide under a pressure of twenty atmospheres. In this condition the tube is heated and graduated. The mercury is then removed, black enamel is rubbed in the scale, and the tube is introduced into a muffle where the scale is brought out clearly in enamel.

This treatment in the muffle has not only the advantage of yielding a permanent scale which resists strong acids, but it also brings about an artificial "ageing" or "seasoning" of the thermometer. In other words, it decreases in a marked degree, the tendency of a thermometer to give too high readings as time goes on. This is evident from the following experimental data:

Thermometers graduated to 360° , which showed ordinarily a rise of 8° – 10° , gave, after this preliminary treatment, when heated for ten hours to 340° – 350° an increase of but 0.6° – 0.8° . Those graduated to 400° showed, under the same conditions, a rise of 1.5° – 2° . In the case of thermometers graduated to 550° the rise under the same conditions was 2° – 3° . After further heating for ten hours the rise was 0.4° – 0.6° . On the contrary, thermometers graduated to 550° , but not exposed to the "seasoning" treatment, showed, after being heated for ten hours, a rise of 16° – 19° , and after a further period of ten hours a rise of 4° – 6° , while further increase was naturally to be expected.

A further improvement of the high temperature thermometer is the coating on the back of the tube which greatly facilitates readings. This same result has been secured in the construction of ordinary thermometers by introducing into the back of the tube a strip of enamelled glass. The difference in the coefficients of expansion renders this impossible in the case of the high temperature thermometers. The strip of enamelled glass has been

replaced, however, very satisfactorily by a simple coating of enamel which is fused upon the surface of the tube at the same time that the figures of the scale are produced. The enamel on the rear of the tube, as well as that of the graduation, are totally unaffected after prolonged exposure to high temperatures.

An extended use of these thermometers is to be expected not only in laboratories, but in many branches of chemical industry, such as tar works, petroleum refineries, anilin works, etc.

I would mention in this connection the great help I have experienced in using Mahlke's "thread thermometer" for obtaining accurate readings at high temperatures. This gives the proper correction for the error due to the projection of a part of the mercury column of the thermometer outside of the substance or confined space, the temperature of which is being measured. In the case of long thermometers and high temperatures this error may reach 30° . Mahlke's thermometer is hung alongside the projecting part of a thermometer in use, and is so arranged as to give at once the reading for the number of degrees to be added to the temperature indicated in order to correct the error mentioned.

ON THE ESTIMATION OF SULPHUR IN PYRITES.¹

BY THOMAS S. GLADDING.

THERE are two recognized methods for the estimation of sulphur in pyrites which, with various modifications, are chiefly used by commercial chemists at the present time. These are:

First, the fusion of the ore with a mixture of sodium carbonate and potassium nitrate, solution in water, filtration from iron hydroxide, and precipitation as barium sulphate.

Second, the solution of the pyrites ore in aqua regia, or in aqua regia and bromine, and subsequent precipitation as barium sulphate.

The following investigation was undertaken to determine the relative merits of these two methods and the proper modifications to be observed:

A chemically pure potassium sulphate was examined for

¹ Read before the New York Section, March 9, 1894.

impurities with negative results. 2.7 grams containing about the amount of sulphur found in one gram of high grade pyrites were dissolved in 300 cc. to 400 cc. water, five cc. concentrated hydrochloric acid added, and a ten per cent. barium chloride solution added, at the rate of one drop per second, to the boiling solution. We obtained after standing over night:

| | |
|---------------|--------------|
| Sulphur | 0.4960 gram. |
| " | 0.4960 " |

Theory requires sulphur 0.4965. This amount of 0.496 gram was taken as the quantity of sulphur contained in 2.7 grams of the potassium sulphate, and the following series of experiments made exactly as above, with the stated additions and modifications. We first investigated the various conditions of the fusion methods.

Series I. With additions of five cc. nitric acid:

| | |
|---------------------|--------------|
| Sulphur found | 0.5007 gram. |
| " " | 0.5007 " |
| " " | 0.5020 " |

The presence of nitric acid produces results too high, from the dragging down of nitrate salts, probably barium nitrate.

Series II. With addition of seventeen grams potassium nitrate:

| | |
|---------------------|--------------|
| Sulphur found | 0.5066 gram. |
| " " | 0.5102 " |

Series III. With addition of fifteen grams of fusion mixture; *viz.*, sodium carbonate and potassium nitrate, and addition of hydrochloric acid to neutrality and five cc. in excess:

| | |
|---------------------|--------------|
| Sulphur found | 0.5005 gram. |
|---------------------|--------------|

Series IV. With addition of potassium chloride, 6.5 grams, sodium chloride, seven grams:

| | |
|---------------------|--------------|
| Sulphur found | 0.4955 gram. |
| " " | 0.4950 " |
| " " | 0.4966 " |

No appreciable error either way.

The above series of experiments show that no *nitric* acid nor nitrates should be present in the solution at the time of precipitation. Series IV shows that when all nitric acid is expelled then sodium chloride and potassium chloride in solution will not cause error. We have found, however, that the complete expulsion of all nitric acid is a very difficult and tedious operation,

requiring repeated evaporations to dryness with excess of hydrochloric acid.

The practical difficulty of removing all the nitric acid, and time and labor required, are serious objections to this method.

The following experiments were made to investigate the conditions of the second or aqua regia method.

Series V. With addition of two grams of citric acid :

| | |
|---------------------|--------------|
| Sulphur found | 0.4960 gram. |
| " " | 0.4960 " |

This shows that the citric acid, which is frequently used to keep up any iron present, does not exert a solvent action.

Series VI. With addition of two grams citric acid, and 0.500 gram iron, which is about the amount of iron in one gram of pyrites ore :

| | | |
|---------------------|-------------|---------------|
| Sulphur found | 0.4934 gram | -0.4937 gram. |
| " " | 0.4937 " | -0.4933 " |
| " " | 0.4940 " | -0.4937 " |
| " " | 0.4938 " | |

This shows that the presence of iron causes low results.

The above results were obtained by ignition of the barium sulphate precipitate at low red heat until the filter paper was thoroughly burned. The precipitate was of a buff color.

On exposing the precipitates to a strong blast for several minutes longer they assumed a decided red color and lost weight.

The results were found to be :

| | |
|---------------------|--------------|
| Sulphur found | 0.4910 gram. |
| " " | 0.4913 " |
| " " | 0.4900 " |

We attribute these erroneous results to the unavoidable dragging down of iron salts (probably iron sulphate) with the barium sulphate, and in place of an equivalent amount of barium sulphate. On ignition, this iron sulphate is decomposed, the sulphuric anhydride is expelled, causing low results, and the remaining iron oxide coloring the residue.

This was corroborated by taking 2.7 grams potassium sulphate, precipitating as above, drying the precipitate, brushing from the paper, drying at about 300° C., and adding the ash of the filter paper which had been burned in a separate dish.

| | |
|---------------------|--------------|
| Sulphur found | 0.4961 gram. |
|---------------------|--------------|

On heating over the blast-lamp for five minutes we found

Sulphur 0.4880 gram.

It is evident that the presence of iron in the solution is incompatible with accurate results.

We next tried the method of Lunge and Hurter. They precipitate the iron with ammonia and throw down the barium sulphate in the filtrate.

Series VII. With addition of 0.5000 gram iron, precipitation of same with ammonia, and precipitation of barium sulphate in the filtrate:

Sulphur found 0.4944 gram.

" " 0.4935 "

These results were too low. On redissolving the ferric hydroxide (on filter paper) with hydrochloric acid, and adding barium chloride to the filtrate, and standing over night, we obtained a precipitate of barium sulphate, giving:

1. Sulphur 0.0020 gram.

2. " 0.0021 "

Adding these amounts we obtained:

Sulphur 0.4964 gram.

" 0.4956 "

The most careful washing failed to wash out all sulphur from the ferric hydroxide, and this solution in hydrochloric acid, and the separate recovery of sulphur contained therein, was found necessary.

These results were the most satisfactory yet obtained. The precipitate of barium sulphate was pure white, pulverulent and did not lose appreciable weight on prolonged heating over the blast-lamp. In this respect it differs from all precipitates hitherto obtained, demonstrates its far greater purity, and gives us a fixed and *final* result.

A method recently published instructs as follows: To the solution (about 200 cc.), heated on a steam-bath and containing twenty cc. free hydrochloric acid "add barium chloride solution from a burette, drop by drop, stirring briskly. Add thirty-five cc. and allow the solution to stand one hour on the steam-bath, filter through ten cm. paper and wash three times with hot water. Ignite and weigh barium sulphate." After calculating per cent.

sulphur, add 0.20 per cent. to the result for solubility of barium sulphate in the acidified liquid.

We tested this method using 2.70 grams potassium sulphate, 200 cc. water, twenty cc. hydrochloric acid, and 0.500 gram iron. We obtained :

| | |
|---------------|--------------|
| Sulphur | 0.4900 gram. |
| " | 0.4898 " |
| " | 0.4902 " |
| " | 0.4894 " |
| " | 0.4905 " |

The average loss was found to be about 0.60 per cent. instead of 0.20 per cent. as stated. The color of the precipitate was light buff. On heating over the blast-lamp for five minutes the precipitate assumed a darker color and lost 0.021 gram in weight so that the percentage of sulphur was reduced about 0.30 per cent. more. Evidently this method does not produce a pure precipitate of barium sulphate.

The following series of comparative analyses on samples of pyrites received for assay, corroborates the above results. The results given under "Fusion Method" were obtained *without* evaporating to dryness to expel all nitric acid. The results given under "Bromine Method, No. 1," were obtained by solution in nitric acid and bromine, evaporation to dryness with hydrochloric acid, taking up with hot water, plus hydrochloric acid, addition of two grams citric acid and precipitation without removing the iron.

In "Bromine Method, No. 2," the iron was removed with ammonia and the barium sulphate precipitated in the filtrate. The ferric hydroxide was dissolved in dilute hydrochloric acid in a separate beaker, heated to boiling, barium chloride added, allowed to stand over night, and the small amount of barium sulphate thus obtained added to the main precipitate.

| Samples. | Fusion method. | Bromine method, Bromine method, | |
|----------|----------------|---------------------------------|--------|
| | | No. 1. | No. 2. |
| I | 52.50 | 51.45 | 51.71 |
| I | 52.34 | 51.30 | 51.73 |
| I | 52.60 | 51.45 | 51.71 |
| I | | 51.34 | 51.71 |
| I | | 51.32 | 51.68 |
| I | | | 51.78 |

| Samples. | Fusion method. | Bromine method, | |
|----------|----------------|-----------------|--------|
| | | No. 1. | No. 2. |
| 2 | 40.92 | | 40.50 |
| 3 | 39.90 | 39.25 | 39.60 |
| 4 | 40.90 | 39.72 | 40.00 |
| 5 | 41.25 | 40.05 | 40.40 |
| 6 | 41.80 | 40.90 | 41.10 |
| 7 | 40.59 | 39.71 | |
| 8 | 42.54 | 41.94 | |
| 9 | 41.41 | 40.40 | |

We see from the above that the "Fusion Method" without expulsion of all nitric acid gives results altogether too high, as was to have been expected.

The "Bromine Method," when iron is not removed, gives results too low by 0.20 per cent. to 0.35 per cent. This is in exact agreement with the previous work on pure potassium sulphate. No accurate allowance can be made on this method as the error will vary with the amount of heat applied in igniting the precipitate of barium sulphate.

In the "Bromine Method, No. 2," the precipitated iron hydroxide was redissolved in every case, and an additional amount of sulphur varying from 0.20 per cent. to 0.30 per cent. was obtained.

The insolubility of barium sulphate in the solution of ferric chloride thus obtained was demonstrated by dissolving 0.027 gram potassium sulphate in fifty cc. water, adding five cc. hydrochloric acid and 0.5 gram iron, precipitating hot and allowing to stand over night. We found:

| | |
|-----------------|--------------|
| 1. Sulphur..... | 0.0049 gram. |
| 2. " | 0.0050 " |
| 3. " | 0.0051 " |

The amount actually present was 0.00496 gram.

As a result of the above investigation and of many comparative analyses of pyrites ores extending over several years, we have adopted the following method of assaying pyrites:

1. Grind the ore to an impalpable powder, dry at 100° C., and keep in well-corked bottles. Ten to fifteen minutes drying is sufficient.
2. Weigh one gram, introduce into beaker, cover with watch-glass, and add ten cc. bromine solution, mix by rotating beaker

and allow to stand ten minutes in the cold. Add ten cc. nitric acid, mix as before, and allow to stand ten minutes longer in the cold. Finally place the beaker on a water-bath, containing cold water, heat slowly to boiling, and when solution becomes quiet remove glass after rinsing and evaporate to dryness. Add ten cc. hydrochloric acid, keeping the beaker covered with a glass, and when violent action ceases, again remove the glass after rinsing, and evaporate to dryness once more. Add one cc. concentrated hydrochloric acid and fifty cc. hot water, digest until solution is complete, filter and wash with hot water. The filtrate, about 100 cc., is now saturated with a slight excess of ammonia, allow to stand hot for ten minutes. The precipitated ferric hydroxide is filtered and washed five or six times more on the paper with boiling hot water, the filtrate acidulated with hydrochloric acid in slight excess, heated to boiling and fifty cc. barium chloride solution added, one drop per second to the boiling liquid. The solution is allowed to stand over night, filtered, washed, and ignited, the precipitate of ferric hydroxide is also dissolved in dilute hot hydrochloric acid heated to boiling, and ten cc. barium chloride solution added. It is allowed to stand over night and the barium sulphate thus obtained added to the main precipitate. One filter paper can be used for the two precipitates.

The bromine solution is prepared by dissolving seventy-five grams potassium bromide in fifty cc. water, adding fifty cc. bromine, stirring and adding water to 500 cc. The bromine will nearly all dissolve. Another form of bromine solution used by some is made by saturating aqua regia with bromine. The first solution is the more certain, however, to oxidize all the ore without separation of any sulphur. The barium chloride is in ten per cent. solution.

Thanks are due to our assistants, Mr. H. E. Cutts and Mr. Thomas Brown, for valuable assistance in the analytical work of the above investigation.

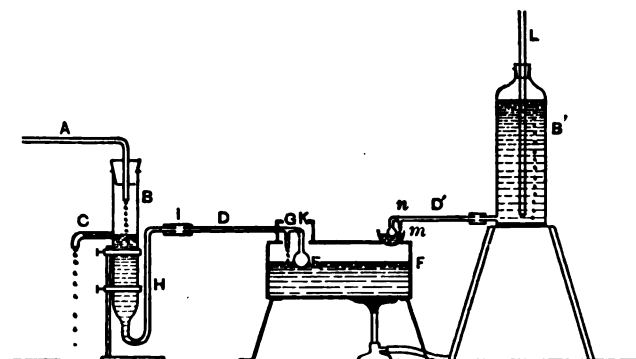
LABORATORY OF STILLWELL AND GLADDING,
NEW YORK.

A CONSTANT LEVEL APPARATUS.

By F. C. ROBINSON.

Received November 18, 1893.

THE following apparatus, which I have used for some time, may interest other chemists; hence the following sketch and description:



B is a glass tube about 2.5 cm. diameter into which is passed the small tube A through a cork. A side tube C extends out about ten cm. and is of much larger bore than A. Upon the lower end of B is sealed a small glass tube H which is bent up until opposite C, and then turned at right angles. Connected with H by a rubber tube is a tube D of equal bore and about twenty-five cm. long. Upon the other end of D is a bulb E, five cm. in diameter, turned down at right angles as shown in the cut. At the point G is a short tube and just beyond it at K, the tube D is closed up by melting it together. F is a water-bath through one of the openings of which E passes and floats upon the water. As the water rises in the bath, E, of course, floats higher, and raises the tube D. The rubber connector holds D upright and allows it to move. If B is clamped so that C and D are upon a level and the tap opened so that water flows into B through A, it will run out of both C and D, but of course D will soon float up so high that no water will run through it, and all will discharge at C. Now heat the bath and as soon as

evaporation has lowered D, sufficiently more water will run into the bath to take the place of that evaporated. A small stream of water flows constantly out at C and into the sink, but it need be very small indeed.

If the bulb E enters the bath through a place needed for evaporations, a small copper cylinder slightly larger than the opening and having a narrow strip cut out of it for D to move up and down in, may be placed over it as in the cut. Of course, the float may be placed in a side tube soldered to the bath with water-connection to it. If one cannot make it of glass it could easily be constructed of metal by any tinman.

I find also that the same idea works admirably for constant feeding of a small platinum dish in evaporating large quantities of water or other liquids for analysis of residues. In such cases the tube D' is directly connected with a bottle holding several liters of water in the manner illustrated in the cut at the right. As D' falls through evaporation of the water in *m*, air enters through L and water drops out at *n* till D' rises so that *n* is higher than the bottom of L when it stops, and thus the level in *m* is constant. In this case the tube D' is very small so that the bulb can be very small and still hold it up. In the one I use, the bulb is only 1.5 cm. in diameter and the tube *n* so close to it that it can be used in a crucible. It is very easy to clean the float from the slight residue clinging to it at the end.

I use the same apparatus for washing precipitates with a large amount of water, placing the bulb in the funnel on the surface of the wash-water.

BOWDOIN COLLEGE,
BRUNSWICK, MAINE, NOVEMBER 18, 1893.

A SCALE OF HARDNESS FOR GLASS.¹

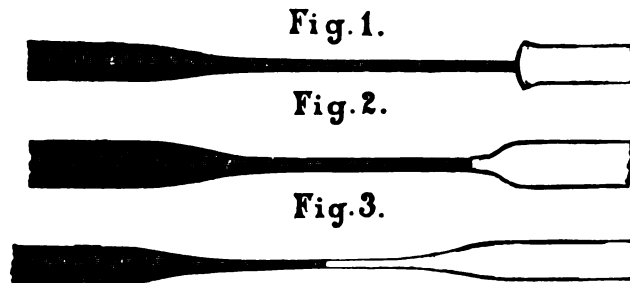
BY W. NIEHLS.

THE term "hardness" as applied to glass, refers to its degree of fusibility in the flame of the blast-lamp. Thus a glass which softens readily in the flame is called a "soft" glass, while one which softens with difficulty is called a "hard" glass. Between the extremes of a very soft and a very hard glass there

¹ Read before the Cincinnati Section, April 16, 1894.

is also quite a series of grades whose differences become very pronounced in actual glass working.

If this difference between two sorts be considerable it is impossible to effect permanent union by fusion between two samples. When the difference is slight, union may be effected between two sorts, but a condition of tension is produced which often causes later, a springing apart at the point of junction, even when not exposed to external strain. Permanent and satisfactory union is accomplished only when the varieties of glass are of the same, or nearly the same, hardness. Practiced glass-blowers make use of this fact in testing the sorts of glass placed at their disposal with reference to their power to unite. Samples of two sorts in the form of small rods are brought together evenly in a small pointed flame, heated therein uniformly, and when soft, fused together by pressure. They are then drawn slowly apart. The softer sample is drawn out more or less easily from the harder, so as to leave a quite pronounced edge when the difference in



hardness is considerable (Fig. 1).

When differences are less marked or are even quite slight, the different lengths of the drawn-out ends are quite noticeable and the dividing line between the two sorts is evident to the eye (Fig. 2).

If the two sorts are of the same hardness both ends are drawn out evenly and there is no line of demarcation (Fig. 3).

Hitherto there has been no systematic classification of glass varieties according to hardness for the convenience of commerce, industry, and science. This lack I have supplied by the arrangement—with the co-operation of the German Physikalisch-

Technische Reichsanstalt—of a well-defined scale of hardness for glass, divided into eight degrees. The following are the typical sorts of glass for each degree:

- I. The softest glass in commerce, French crystal:
- II. Soft Thuringian glass, used for artificial flowers, toys, etc., English crystal.
- III. Hard Thuringian glass, as used for thermometers, finer apparatus, etc.
- IV. Jena normal thermometer glass (XVI^{'''} of Schott and Co.).
- V. French hard crystal used in Paris for normal thermometers (by Tonnelot).
- VI. Jena boro-silicate thermometer glass (59^{'''} of Schott and Co.).
- VII. Jena thermometer glass free from alkalies (122^{'''} of Schott and Co.). Both VI and VII are used for high temperature thermometers and many other purposes.
- VIII. Cavalier's Bohemian crystal glass, used for combustion tubes, etc.

Normal scales of hardness for glass, arranged according to the above scheme, have been prepared and can be secured through dealers in chemical apparatus. They contain on cardboard, illustrative samples of the results of fusing (as described above), each number in the series with the next following number. Compartments also are well stocked with small rods of each degree on the scale—each rod stamped with its number—to be used for testing.

The use of such a scale brings a most desirable element of certainty into the glass trade as well as into the technique of physical and chemical laboratories, and many industrial operations.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 6.]

A METHOD OF DETERMINING THE KOETTSTORFER FIGURE OF DARK-COLORED SUBSTANCES.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received May 5, 1894.

THE Koettstorfer figure of a fat or resin is the number of milligrams of potassium hydroxide required to saponify one gram of the substance. It is determined by adding to a

weighed quantity of the substance a measured excess of an alcoholic solution of potash, evaporating off the alcohol, redissolving in neutral alcohol, and determining the excess of potash by standard hydrochloric acid. When the substance is light in color and the alcohol free from aldehyde, the determination is easily made, but if the substance has much color of its own the end reaction with phenolphthalein is indistinct. The same is true if the alcohol used contains aldehyde, as this gives with caustic potash a red-brown color. The latter difficulty can be surmounted by purifying the alcohol, but the former one is more serious. In experimenting to find a mode of procedure which would obviate the difficulty it was observed that a solution of neutral soap, to which ammonium chloride had been added, when submitted to distillation liberated a quantity of ammonia equivalent to the alkali combined with the soap.

Based on this principle the following method was devised: Two grams of the substance under examination is weighed into an Erlenmeyer flask, an excess of an alcoholic solution of caustic soda added, and the alcohol evaporated off. 250 cc. of ninety-three per cent. alcohol is now added and the solution heated until the soap is dissolved. Carbonic acid gas is now passed through the solution for about one hour. This treatment converts the free caustic alkali present into carbonate and bicarbonate which precipitate. The solution is then filtered into a suitable flask and most of the alcohol distilled off. It is necessary to add a spiral of platinum wire or a piece of sharp pointed metal or glass to prevent boiling over. When most of the alcohol is gone a solution of ten grams of ammonium chloride, in 100 cc. of water, is added and the solution distilled as far as possible, the distillate being caught in twenty cc. of normal hydrochloric acid which is titrated at the end of the operation, using methyl orange as indicator. The amount of hydrochloric acid neutralized by ammonia is equivalent to the combined alkali in the test.

Alcohol of ninety-three per cent. was found to dissolve sodium bicarbonate sufficient to neutralize 0.34 cc. of normal acid for every 100 cc. of alcohol used. A deduction must therefore be made for this in the calculation.

A sample of linseed-oil tested in this way gave a Koettstorfer

figure of 192.4, and by the ordinary process the figure found was 193.1. A sample of dragon's blood resin gave 124.9.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY
OF CINCINNATI. XLV.]

ON THE VOLATILITY OF BORAX,¹

BY SIGMUND WALDBOTT, PH.D.

THE fact that borax is a volatile substance under ordinary laboratory conditions seems to have, hitherto, escaped notice. No reference is made to it in the literature of pure chemistry, and the following quotation from E. Cramer² would imply a general belief among technical chemists to the contrary:

"The boric acid must not be added in the form of vitreous boric acid, but in the form of sodium borate, whereby no volatilization will take place."

In the course of an investigation on the borates, carried on in connection with Prof. T. H. Norton, certain observations led to the suspicion that borax was not entirely unaffected by the heat of the ordinary blast-lamp.

A series of quantitative experiments was made, the results of which may be briefly summarized as follows:

If a small amount of pure borax, say four grams, be heated in a platinum crucible of fifty cc. contents, until the water of crystallization is quantitatively given off, and if the residue, borax glass, then be heated over a Bunsen burner for about ten minutes or longer, the weight will be found constant. If the crucible, half covered by the lid, be next heated over a gentle blast-flame, there will be noticed a very slight, yet distinctly perceptible loss in weight, increasing in proportion to the intensity of heat and the time of heating.

If now the uncovered crucible with its contents be subjected to an intense white heat, heavy vapors arise from the surface of the molten borax glass, and if heating is prolonged a very marked decrease in weight becomes evident.

The following experimental results are classified according to the general temperature maintained:

¹ Read before the Cincinnati Section, February 15, 1894.

² E. Cramer, *Thonindustrie-Zeitung*, 1892, p. 155.

A. VOLATILITY AT HIGHER TEMPERATURES.

The experiments recorded under this heading were all carried out at a white heat, as high a temperature as could be obtained by the ordinary laboratory blast-lamp. The borax used in these experiments, unless expressly stated otherwise, was purified by recrystallization and by drying for about twelve hours on unglazed porcelain.

I.

1.2500 grams $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$, when heated, lost 0.5968 gram $\text{H}_2\text{O} = 47.74$ per cent. (Theoretical loss = 47.12 per cent., drying on unglazed porcelain was omitted.)

0.6532 gram borax glass remained and was heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---------------------------|------------------------------|-----------------------|-------------------|-------------------------|
| 5 | Crucible uncovered..... | 0.0055 | 0.0055 | 0.8 |
| 7 | “ covered | 0.0010 | 0.0065 | 1.0 |
| 10 | “ uncovered | 0.0060 | 0.0125 | 2.0 |
| 7 | “ half covered, chimney used | 0.0039 | 0.0164 | 2.5 |
| 10 | “ uncovered | 0.0054 | 0.0218 | 3.3 |
| 5 | “ “ | 0.0050 | 0.0268 | 4.1 |
| 2 | “ “ | 0.0009 | 0.0277 | 4.2 |

0.6532 gram borax glass lost 4.2 per cent. in forty-six minutes.

II.

7.9201 grams $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$, when heated, lost 3.7356 grams $\text{H}_2\text{O} = 47.17$ per cent. (Theoretical loss = 47.12 per cent.)

4.1845 grams borax glass remained and were heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---------------------------|-------------------------------------|-----------------------|-------------------|-------------------------|
| 5 | Crucible open..... | 0.0085 | 0.0085 | 0.23 |
| 10 | “ half covered | 0.0040 | 0.0125 | 0.298 |
| 10 | “ “ “ chimney used | 0.0045 | 0.0170 | 0.406 |
| | Lid, covered with drops, was heated | 0.0023 | 0.0193 | 0.461 |
| 10 | Crucible open..... | 0.0080 | 0.0273 | 0.652 |
| 10 | “ “ | 0.0076 | 0.0349 | 0.834 |

4.1845 grams borax glass lost 0.83 per cent. in forty-five minutes.

In comparing the results of these two experiments it will be seen that the absolute amount of borax evaporated in a given time is about the same in both cases, whether a large or a small quantity is used, indicating that the amount volatilized at a given high temperature depends chiefly on the surface of the fused mass.

In the following three experiments it was sought to determine in what form borax is volatile.

It is possible that either borax is volatile as such, or that it is dissociated at high temperatures, giving off B_2O_3 and leaving Na_2O behind. An analysis of the residue after heating borax glass for a certain length of time would decide; for in case B_2O_3 is evolved the percentage of Na_2O must be higher than if borax as such is volatilized. As the difference between the two values for Na_2O under the latter supposition would increase rapidly with the loss in weight, samples of borax glass were heated long enough to bring about a loss of some twelve per cent.

III.

1.5630 grams $Na_2B_4O_7 \cdot 10H_2O$, lost on heating 0.7380 gram $H_2O = 47.21$ per cent. (Theoretical loss = 47.12 per cent.)

0.8250 gram borax glass remained and was heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---------------------------|--|-----------------------|-------------------|-------------------------|
| 20 | Crucible partly covered | 0.0106 | 0.0106 | 1.3 |
| 20 | Crucible covered, small space allowed, fine drops on lid | 0.0020 | 0.0126 | 1.6 |
| | The lid alone was heated | 0.0060 | 0.0186 | 2.3 |
| 20 | Crucible uncovered | 0.0171 | 0.0357 | 4.4 |
| 60 | Crucible uncovered | 0.0365 | 0.0722 | 8.8 |
| 60 | Crucible uncovered, heat less intense | 0.0210 | 0.0932 | 11.34 |

0.8250 gram borax glass lost 11.34 per cent. in three hours.

The residue weighed 0.7318 gram, and was analyzed, yielding 0.2185 gram Na_2O or 29.85 per cent.

| | Theory, if loss were B_2O_3 . | Theory, if loss were $Na_2B_4O_7$. | Found. |
|---------------|---------------------------------|-------------------------------------|-----------------|
| Na_2O | 34.62 per cent. | 30.69 per cent. | 29.85 per cent. |

IV.

1.5691 grams $Na_2B_4O_7 \cdot 10H_2O$, lost on heating 0.7387 gram $H_2O = 47.07$ per cent. (Theoretical loss = 47.12 per cent.)

0.8304 gram borax glass remained and was heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---------------------------|---------------------|-----------------------|-------------------|-------------------------|
| 30 | Crucible open | 0.0134 | 0.0134 | 1.6 |
| 90 | " " | 0.0565 | 0.0699 | 8.4 |
| 35 | " " | 0.0220 | 0.0919 | 11.07 |
| 20 | " " | 0.0121 | 0.1040 | 12.52 |

0.8304 gram borax glass lost 12.52 per cent. in about three hours.

The residue weighed 0.7264 gram, and yielded on analysis 0.21796 gram Na_2O .

| | Theory, if loss
were B_2O_3 . | Theory, if loss
were $\text{Na}_2\text{B}_4\text{O}_7$. | Found. |
|-----------------------------|--|---|-----------------|
| Na_2O | 35.09 per cent. | 30.69 per cent. | 30.01 per cent. |

The low results obtained for Na_2O in III and IV were found to be due to a slight loss liable to be incurred in the analytical process used (treatment with ammonium fluoride), which will be touched upon in a communication following this. This source of error was obviated in the following experiment :

V.

0.9350 gram borax glass was heated as follows :

| Time of
heating.
minutes. | Mode of heating. | Loss each
time,
gram. | Total
loss,
gram. | Total
loss in
per cent. |
|---------------------------------|-------------------------|-----------------------------|-------------------------|-------------------------------|
| 60 | Crucible uncovered..... | 0.0387 | 0.0387 | 4.1 |
| 120 | " " | 0.0914 | 0.1301 | 13.91 |

0.9350 gram borax glass lost 13.91 per cent. in three hours.

The residue weighed 0.8049 gram, and yielded on analysis 0.2439 gram Na_2O .

| | Theory, if loss
were B_2O_3 . | Theory, if loss
were $\text{Na}_2\text{B}_4\text{O}_7$. | Found. |
|-----------------------------|--|---|-----------------|
| Na_2O | 35.65 per cent. | 30.69 per cent. | 30.31 per cent. |

These results show beyond doubt that borax is volatile as such, and are corroborated by the following observations :

A thin film of borax glass on the inside of a crucible can be entirely volatilized by persistent heating.

The drops which occasionally gather on the lid of the crucible in the experiments described, can also be driven off completely by continued heating.

SUMMARY OF THE RESULTS OF EXPERIMENTS A, I-V.

| Losses in
per cent. at
the end of | WEIGHTS OF BORAX GLASS. | | | | |
|---|-------------------------|-------------------------|-------------------------|------------------------|-----------------------|
| | I,
0.6532
gram. | II,
4.1845
grams. | III,
0.8250
gram. | IV,
0.8304
gram. | V,
0.9350
gram. |
| 5 minutes..... | 0.8 | 0.23 | ... | ... | ... |
| 12 " | 1.0 | | ... | ... | ... |
| 15 " | ... | 0.298 | ... | ... | ... |
| 20 " | ... | | 1.3 | ... | ... |
| 22 " | 2.0 | | ... | ... | ... |
| 25 " | ... | 0.461 | ... | ... | ... |
| 29 " | 2.5 | | ... | ... | ... |
| 30 " | ... | | ... | 1.6 | ... |
| 35 " | ... | 0.652 | ... | ... | ... |

| Losses in
per cent at
the end of | WEIGHTS OF BORAX GLASS. | | | | |
|--|-------------------------|-------------------------|-------------------------|------------------------|-----------------------|
| | I,
0.6532
gram. | II,
4.1845
grams. | III,
0.8250
gram. | IV,
0.8304
gram. | V,
0.9350
gram. |
| 39 " | 3.3 | | ... | ... | ... |
| 40 " | ... | | 2.3 | ... | ... |
| 44 " | 4.1 | | ... | ... | ... |
| 45 " | ... | 0.834 | ... | ... | ... |
| 46 " | 4.2 | | ... | ... | ... |
| 60 " | ... | | 4.4 | ... | 4.1 |
| 120 " | ... | | 8.8 | 8.4 | ... |
| 155 " | ... | | ... | 11.07 | ... |
| 175 " | ... | | ... | 12.52 | ... |
| 180 " | ... | | 11.34 | ... | 13.91 |

These values obtained for the volatility of borax at high temperatures suggested the study of the behavior of borax glass at a lower heat, with the following results:

B. VOLATILITY AT LOWER TEMPERATURES.

I.

4.0199 grams $\text{Na}_2\text{B}_4\text{O}_{10} + 10\text{H}_2\text{O}$ were heated in a platinum crucible until the water was expelled and the weight was constant.

Water expelled = 1.887 grams = 46.96 per cent. (Theoretical loss = 47.12 per cent.)

2.1320 grams borax glass remained and were further heated as follows:

| Time of
heating,
minutes. | Mode of heating. | Loss each
time.
gram. | Total
loss,
gram. | Total
loss in
per cent. |
|---------------------------------|--|-----------------------------|-------------------------|-------------------------------|
| 10 | Bunsen burner with chimney, full
flame | 0.0000 | 0.0000 | 0.000 |
| 15 | Moderate blast-flame, crucible half
covered | 0.0014 | 0.0014 | 0.065 |
| 15 | Moderate blast-flame, crucible half
covered, drops noticed on lid | 0.0008 | 0.0024 | 0.112 |
| 20 | Moderate blast-flame, crucible half
covered, drops noticed on lid | 0.0020 | 0.0044 | 0.206 |
| 5 | Strong blast-flame, crucible open ... | 0.0048 | 0.0092 | 0.431 |
| 10 | " " " " " ... | 0.0073 | 0.0165 | 0.774 |
| 60 | Bunsen burner, full flame, crucible
half covered | 0.0000 | 0.0165 | 0.774 |

II.

2.4425 grams borax glass were heated for ten minutes over a strong blast-flame in order to insure perfect expulsion of water.

It weighed then 2.4327 grams and was further heated as follows :

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---------------------------|---|-----------------------|-------------------|-------------------------|
| 30 | Bunsen burner, strong flame, crucible half covered..... | 0.0000 | 0.0000 | 0.000 |
| 15 | Gentle blast-flame, crucible half covered..... | 0.0015 | 0.0015 | 0.061 |
| 15 | Gentle blast-flame, crucible half covered..... | 0.0017 | 0.0032 | 0.131 |

III.

0.6148 gram borax glass after being heated for a short time over a strong blast-flame, weighed 0.6126 gram and was further heated as follows :

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---------------------------|--|-----------------------|-------------------|-------------------------|
| 15 | Stronger blast-flame, crucible half covered..... | 0.0034 | 0.0034 | 0.555 |
| 15 | Gentle blast-flame, crucible half covered..... | 0.0016 | 0.0050 | 0.816 |
| 15 | Gentle blast-flame, crucible half covered..... | 0.0018 | 0.0068 | 1.110 |

SUMMARY OF THE RESULTS OF EXPERIMENTS B, I-III.

| Weight of borax glass. | Loss in per cent. at the end of | | | |
|------------------------|---------------------------------|-----------------------|-----------------------|-----------------------|
| | 15 minutes, per cent. | 30 minutes, per cent. | 45 minutes, per cent. | 50 minutes, per cent. |
| 2.1320 grams..... | 0.065 | 0.112 | | 0.206 |
| 2.4327 " | 0.061 | 0.131 | | |
| 0.6126 gram..... | 0.555 | 0.816 | 1.110 | |

The question here suggests itself how this behavior of borax might influence the accuracy of such determinations of boric acid as involve exposure of a borate to high temperatures, as for example in the determinations of boric acid by the methods of H. Rose and G. Schaffgotsch. (v. Fresenius Quant. Anal.)

As in these determinations borates of a higher basicity than borax are formed, the results just given, cannot be with certainty utilized, although the more basic borates are probably less volatile than borax. But even supposing these more basic borates to be as volatile as borax itself, a material error from this source can occur only, if there be but a small amount of the borate subjected to analysis, and if the expulsion of carbon dioxide be attempted at too high a temperature and maintained for an unduly long time.

To illustrate such an exceptional case let us refer for instance to the experiment under A I, where it is shown that 0.6532 gram borax glass lost in weight 0.0125 gram=two per cent., when exposed to a white heat for twenty-two minutes, while the crucible was uncovered for fifteen minutes.

If, therefore, 0.2805 gram boron trioxide be analyzed by the method of G. Schaffgotsch this amount would be equivalent to 0.6532 gram of the borate $B_2O_3Na_2$ formed in this process; this salt would lose in weight two per cent. in twenty-two minutes, if exposed to a white heat, if we assume that it be exactly as volatile as borax under the same conditions.

There would then remain 0.6401 gram of the borate, containing 0.2749 gram of B_2O_3 , which implies a loss of B_2O_3 equal to 0.0056 gram or 1.99 per cent.

It is, however, evident from the above that a loss from volatilization of the borate will fall within the errors of manipulation, when in an analysis a normal amount of boric acid is taken, say not less than one gram and when the heating is maintained for about ten minutes at not too high a temperature. This is under the assumption that borates of a higher basicity than borax are volatile to the same extent as the latter. Whether this is the case or not I have not attempted to ascertain, but a preliminary experiment made with a borate of approximately the composition $B_2O_3Na_2$ shows that an increase of basicity in the molecule of borax does not guard the more basic borate from volatilization entirely, for I observed with this borate the same phenomena noticeable when heating borax; *viz.*, the evolution of heavy vapors from its surface, implying a loss in weight when subjected to a white heat. A statement contrary to this fact was made by G. Schaffgotsch¹ in claiming that the salt formed by the action of one and a half molecules of Na_2CO_3 on one molecule of B_2O_3 [$=B_2O_3Na_3$] is "gewichtsbeständig."

Prof. Karl Langenbeck, of Zanesville, Ohio, kindly consented to carry out some experiments on the volatilization of borax on a large scale in kilns, making use of pyrometers. With the approval of Prof. Langenbeck, I herewith add his interesting

¹ G. Schaffgotsch, *Pogg. Ann.*, 107, 427. Ueber die Bestimmung der Borsäure und über die Flüchtigkeit der Borsäure.

communications on the subject which are in perfect accord with the results obtained in the laboratory.

I. JANUARY 30, 1894.

12.3036 grams of borax glass were placed in a small platinum dish and set in a fire-clay capsule four inches in diameter and four inches deep, and this placed next to the pyrometers of a kiln.

From incipient redness to the melting down of Seger's pyrometric cone No. 9, took about forty-eight hours when the firing was discontinued and the kiln allowed to cool, which in about twelve hours, was no longer red.

In other words the borax glass was at a red heat about sixty hours, and reached the temperature of the melting point of Seger's pyrometric cone No. 9, ($=1410^{\circ}\text{C.}$). On removal from the kiln the inside of the clay capsule was heavily glazed and the borax glass in the platinum dish found to weigh 6.2776 grams, hence 6.0260 grams had been volatilized, or 48.98 per cent.

II. FEBRUARY 6, 1894.

5.7698 grams $\text{Na}_2\text{B}_4\text{O}_{10}$, exposed to the heat of Seger's pyrometric cone No. 7 (1350°C.) lost 1.2926 grams or 22.40 per cent. This heat took ten hours less to reach and cooled about two hours more quickly, hence the specimen was about twelve hours less under a red heat.

9.2036 grams $\text{Na}_2\text{B}_4\text{O}_{10}$, exposed to the heat of the melting point of an alloy fifteen per cent. Ag, eighty-five per cent. Au (about 1050°C.) lost 0.7259 gram or 7.88 per cent.

To reach this heat from very low redness took about twenty hours, and the cooling to blackness six hours.

It looks very much as if it did not take so very much heat to begin the volatilization, and that the duration of fire rather than the temperature determines the amount of loss.

III. FEBRUARY 13, 1894.

7.5803 grams borax glass were exposed in a platinum dish to a heat, which was just sufficient to melt silver (954°C.) and by careful regulation of the gas this temperature was held, within very narrow limits for three hours.

The furnace is an up and down draught made by Geith, of Coburg, Germany, from designs of Seger, and has a zone of at least seventy-five cubic inches that is perfectly uniform in heat. The dish of borax glass and the pyrometric trials were placed in the center of this zone.

The dish lost in three hours 0.1115 grams or 1.47 per cent.

SUMMARY OF THE RESULTS OBTAINED BY PROF. LANGENBECK.

| Amount of borax glass, grams. | Duration of heat, hours. | Maximum temperature. | Means of measuring the temperature. | Loss, grams. | Loss in per cent. |
|-------------------------------|--------------------------|----------------------|-------------------------------------|--------------|-------------------|
| 12.3036 | 60 | 1410° C. | Seeger's cone, No. 9. | 6.0260 | 48.98 |
| 5.7698 | 48 | 1350° C. | Seeger's cone, No. 7. | 1.2926 | 22.40 |
| 9.2036 | 26 | 1050° C. | Alloy 15 % Ag 85 % Au. | 0.7259 | 7.88 |
| 7.5803 | 3 | 954° C. | Ag. | 0.1115 | 1.47 |

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI. XLVI.]

ON THE VOLATILITY OF SODIUM FLUORIDE.¹

By SIGMUND WALDBOTT, PH.D.

THE analyses mentioned in Experiments A III and A IV of the foregoing communication did not at first give perfectly satisfactory results. In the endeavor to ascertain the cause of the deficiency, the analytical method employed was subjected to a careful examination.

This method, as described by A. Reischle,² is based on the principle that boric acid can be easily driven off from a borate by mixing it with six times its weight of resublimed ammonium fluoride, and heating carefully until all the boron is volatilized as ammonium borofluoride.

The residue, consisting of the fluorides of the metals that were combined with boric acid, is then treated with sulphuric acid and evaporated to dryness. The sulphates are ignited and weighed, and the amount of boric acid, if desired, is calculated from the difference between the original weight and the weight of the oxides present in the sulphates.

¹ Read before the Cincinnati Section, February 15, 1894.

² A. Reischle, *Ztschr. anorg. Chem.*, 4, 111-116. Abst. in *J. Chem. Soc.*, 1893, (abstracts) p. 491.

This process, according to comparative tests made by Reischle, has proved to be the best of all known methods for determining boric acid indirectly. Several analyses carried out in the laboratory of the University of Cincinnati confirm its reliability.

Experience shows, however, that a few precautions must be closely observed in order to insure accurate results.

The ammonium fluoride employed must be resublimed, or at least the residue left on sublimation must be carefully determined and the necessary deduction made from the final weighing.

Another source of possible error seemed to lie in the volatility of the alkaline fluorides at a comparatively low temperature, and some abnormal results recorded by Reischle, were probably due to this cause.

As nothing has been published on this subject it seemed desirable to examine closely the behavior of sodium fluoride, at least at varying temperatures, and bring the results of the study to bear upon the details of the Reischle method.

The sodium fluoride employed was chemically pure and procured from C. Schuchardt in Görlitz.

The following experimental results were obtained:

I.

NaF not dried, = 0.5605 gram.

Heated over the Bunsen burner, = 0.5495 gram.

Heated again for two minutes, = 0.5490 gram.

This weight, 0.5490 gram of dry NaF, was further heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---------------------------|--|-----------------------|-------------------|-------------------------|
| 2 | Moderate blast flame..... | 0.0040 | 0.0040 | 0.71 |
| 6 | Bunsen burner with chimney, crucible slightly uncovered..... | 0.0020 | 0.0060 | 1.09 |
| 2 | Blast-flame, crucible uncovered..... | 0.0167 | 0.0227 | 4.1 |
| 12 | Bunsen burner with chimney, crucible slightly uncovered..... | 0.0060 | 0.0287 | 5.2 |

II.

NaF not dried, = 0.2775 gram.

Heated over Bunsen burner to constant weight, = 0.2714 gram.

This weight, 0.2714 gram of dried NaF, was further heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Loss in per cent. |
|---------------------------|---|-----------------------|-------------------|-------------------|
| 6 | Bunsen burner, crucible slightly uncovered | 0.0039 | 0.0039 | 1.4 |
| 5 | Bunsen burner, crucible slightly uncovered | 0.0034 | 0.0073 | 2.7 |
| 5 | Bunsen burner, lid off, contents half melted | 0.0047 | 0.0120 | 4.4 |
| 10 | Small flame, bottom just red hot, crucible slightly covered | 0.0010 | 0.0130 | 4.9 |
| 15 | Same, but flame slightly reduced | 0.0003 | 0.0133 | 4.9 |

It follows from these experiments that the full flame of a Bunsen burner, if applied to 0.549 gram of sodium fluoride, will cause a loss of nearly 0.4 per cent. in six minutes, and if applied to 0.2714 gram will cause a loss of 1.4 per cent. in six minutes, while if the flame be reduced so that it will hardly redden the bottom of the covered platinum crucible there will be no very appreciable loss in fifteen minutes.

By observing these two precautions—subjecting sufficient material to analysis to yield not less than 0.6 gram sodium fluoride and applying as little heat as possible—the Reischle method gives excellent results, and the slight discrepancy between the results of the analysis in Experiment A V of the preceding paper, executed after the fact of the volatilization of sodium fluoride was ascertained, and the results of the analyses in experiments A III and A IV is readily accounted for.

In conclusion I wish to express to Prof. Norton my sincerest thanks for the many courtesies extended to me during these experiments. I feel likewise much indebted to Prof. Langenbeck for his kindness in having carried out the experiments on a larger scale as before recorded.

CINCINNATI, MARCH 21, 1894.

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND HENRY E. SPENCER.

Received May 5, 1894.

I. SILVER FROM COPPER.

THE literature relating to electrolysis contains two suggestions bearing upon the separation of these metals. The first is that of Classen, (*Quantitative Analyse durch Elektrolyse, dritte Auflage*, p. 124). In reality this is not an electrolytic method

as the author proposes to first separate the metals by precipitating out the silver as oxalate, filtering off the same, dissolving it in potassium cyanide, and then decomposing this solution of the double cyanide of silver and potassium by means of the electric current. The double oxalate of copper and ammonium being soluble in water is filtered from off the insoluble silver oxalate, and the copper is then deposited from this solution by the current. No data obtained in the actual use of the method appear to have been published. The insolubility of silver oxalate in ammonium oxalate is not generally conceded (Rose, *Analyt. Chemie*, 1, 342), so that it might well be expected, if this statement be true, that the deposit of copper would contain silver. Experiments were instituted to ascertain how accurate the method really was. The results of a few are given below. They are at the least quite instructive.

Experiment 1.—Ten cc. of a cold saturated solution of ammonium oxalate were added to a solution containing fifty cc. of copper sulphate (= 0.2284 gram of metallic copper) and ten cc. of silver nitrate (= 0.1000 gram of metallic silver). The precipitated silver oxalate was filtered and washed with ten cc. of an ammonium oxalate solution and later with pure water. The washings were colorless and the filtrate was perfectly clear, not the slightest turbidity being observed. The liquid, now 200 cc. in volume, was heated to 50° C., and electrolyzed with a current of 3-4 cc. of electrolytic gas per minute. This procedure was as nearly like that prescribed by Classen (*Elektrolyse*, pp. 78, 124) as it could be, since that chemist fails to give details, leaving the same to the student for adjustment. The precipitation of the copper was rapid and in every respect satisfactory. The deposit of copper weighed 0.2285 gram. Apparently the separation was complete and in no way lacking. However, upon dissolving the copper in dilute nitric acid, diluting with water and adding dilute hydrochloric acid a decided cloudiness was produced. This was found to be *due to silver chloride*.

Experiment 2.—In this trial the quantity of copper was reduced to 0.1142 gram. The silver present equaled 0.1 gram. Twenty-five cc. of ammonium oxalate were used for the precipitation and eleven more for the washing. In other respects the

conditions were similar to those in Experiment 1. The copper deposit weighed 0.1140 gram, instead of 0.1142 gram as required by theory, *yet it contained a very decided amount of silver*, which was revealed upon examining the copper.

Experiment 3.—The details here were analogous to those in Experiment 1. The precipitated copper weighed 0.2283 gram, *but after solution gave 0.0012 gram silver chloride equal to 0.0009 gram metallic silver.*

Experiment 4.—This was similar to experiment 2. The precipitate of copper weighed 0.1134 gram. It was 0.0008 gram low, but notwithstanding it showed on examination the presence of 0.0009 gram of silver.

Many more trials were made with varying amounts of copper, silver, and ammonium oxalate, but in every instance silver showed itself upon examining the precipitated copper. The inevitable conclusion is then that, however insoluble silver oxalate may be in the absence of other metals when copper is present with it, weighable amounts do pass into solution. Care was taken not to electrolyze solutions that were not absolutely clear. At times great difficulty was experienced in getting a clear filtrate from the silver oxalate. All cloudy filtrates were rejected. The results given above demonstrate that the suggestion of Classen (*loc. cit.*) with reference to the separation of silver and copper is not entitled to any consideration on the part of those who are engaged in electrolytic studies.

From an article published in the *Ztschr. angew. Chemie*, 696 (1892), by Rüdorff, it would seem that this chemist also failed, in using Classen's method, to obtain satisfactory results. The experiments in this communication are, therefore offered as a confirmation of Rüdorff's observations so far as concerns the separation of silver and copper.

The second suggestion in regard to the electrolytic separation of these two metals was offered by Smith and Frankel (*J. Frank. Inst.*, 1889; Smith's *Electrochemical Analysis*, p. 100). They electrolyzed a solution containing the double cyanides in the presence of an excess of alkaline cyanide. Numerous repetitions of their method, made in this laboratory, confirm their observation. Rüdorff (*loc. cit.*) also found it satisfactory. **The time-**

factor can, as will be noticed below, be much reduced by merely electrolyzing the solution at a temperature ranging from 65° to 70° C. The method in consequence is rendered more serviceable. Results obtained in this way follow:

Experiment 1.—A solution under electrolysis contained 0.1 gram of metallic silver and 0.1140 gram of metallic copper. The quantity of potassium cyanide present equaled 1.8 grams. The temperature of the liquid was maintained at 65° C., throughout the entire decomposition. The current was $N.D_{100}=0.07$ ampere. The total dilution of the solution equaled 200 cc. The time required for the complete precipitation of the silver was about three hours. The deposit weighed 0.0996 gram; it did not contain copper.

Experiment 2.—In this trial the conditions were similar to those in Experiment 1. The silver deposit weighed 0.1 gram. It contained no copper.

A silver dime was dissolved and the solution diluted to a definite volume. Twenty-five cc. of this solution contained 0.1081 gram of metallic silver. One gram of potassium cyanide was added to the solution and the whole then diluted to 200 cc. The temperature of the liquid during the electrolysis was 60° C. The time of precipitation occupied three hours. The silver deposit weighed 0.1080 gram; it was free from copper.

Fifty cc. of the coin solution ($=0.2162$ gram of metallic silver) were mixed with two grams of potassium cyanide, diluted with water to 225 cc., heated to 65° C., and electrolyzed with a current of $N.D_{100}=0.07$ ampere. The precipitated silver weighed 0.2153 gram.

The method of Smith and Frankel, as thus modified is applicable where results are desired in a comparatively short time-period.

2. MERCURY FROM COPPER.

These metals were also fully separated from each other by the electrolytic decomposition of their double cyanide solution (Smith and Frankel, *Am. Chem. J.*, **11**, 264, 104; Smith and McCauley, *J. Anal. Appl. Chem.*, **5**, 489, and *Ber. d. chem. Ges.*, **24**, 2936; also Freudenberg, *Ztschr. phys. Chem.*, **12**, 113). No difficulty attends the separation, and possibly the only objection

that could be offered to the method is, that considerable time is required for its completion. As in the case of silver and copper it is only necessary to apply a gentle heat to the solution undergoing electrolysis and the time-factor will be greatly reduced. For example :

Experiment 1.—A solution of 200 cc. volume, containing 0.2167 gram of metallic mercury, 0.2156 gram of metallic copper, and two grams of potassium cyanide was heated to 65° C. and electrolyzed with a current of $N.D_{100} = 0.08$ ampere. The precipitation was finished in three and one-half hours. The deposit of mercury was adherent and weighed 0.2168 gram. It contained no copper.

Experiment 2.—Here the conditions were nearly like those in (1). The current of $N.D_{100} = 0.06$ ampere acted for a period of four hours. The precipitated mercury weighed 0.2169 gram, but it did not contain copper.

Experiment 3.—The temperature of the solution was 70° C. The current of $N.D_{100} = 0.08$ ampere acted through four hours. The mercury weighed 0.2170 gram. It contained no copper.

Experiment 4.—In this trial the quantity of each metal was half the amount given in the preceding experiments. But one gram of potassium cyanide was present. The current of $N.D_{100} = 0.08$ ampere acted three hours upon the solution heated to 70° C. The precipitated mercury weighed 0.1083 gram. Copper was not found in it.

3. SILVER FROM CADMIUM.

These metals have usually been separated electrolytically when present in nitric acid solution. As both are precipitated by rather feeble currents form solutions containing them as double cyanides, it did not occur to the writers until recently that they could also be separated from each other in a solution of this nature. The two experiments which follow show that such is indeed the case. The separation cannot be made in a cold solution. The silver will always be contaminated with cadmium. The most favorable conditions are noted in the examples here given.

Experiment 1.—A solution of 200 cc. volume contained 0.1000 gram of metallic silver, a like quantity of metallic cadmium, and

three grams of potassium cyanide. It was heated to 65° and then electrolyzed for three and one-half hours with a current of $N.D_{100} = 0.04$ ampere. The precipitated silver weighed 0.1004 gram. No cadmium was found in it. The poles were separated two inches from each other.

Experiment 2.—Operating with conditions just like those in experiment 1, the deposit of silver weighed 0.0999 gram.

UNIVERSITY OF PENNSYLVANIA,
April 23, 1894.

THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON MOLYBDENUM TRIOXIDE.

BY EDGAR F. SMITH AND GEORGE W. SARGENT.

Received May 5, 1894.

THE action of phosphorus pentachloride upon the trioxides of tungsten and of molybdenum has been the subject of investigation by Schiff,¹ Teclu,² and Piutti.³ Schiff announced that with tungstic acid and the pentachloride the products were in the main phosphorus oxychloride and a brown colored tungsten oxychloride. Teclu, upon repeating Schiff's experiments, obtained phosphorus oxychloride and the *hexachloride of tungsten*. This was the result when working with one part of WO_3 and three parts of phosphorus pentachloride. The mixture was heated in sealed tubes. Piutti substituted molybdenum trioxide and hoped to get a corresponding molybdenum *hexachloride*. This he did not realize; instead, he obtained a compound which gave results on analysis that led to the formula $MoCl_5 \cdot POCl_3$. Along with the dark-green colored crystals of this compound there was a reddish-brown liquid. The tube, after being opened, and as soon as the liquid was removed, was connected with a Woulff bottle to which a drying tube was attached. The other end of the sealed tube was opened and connected with a carbon dioxide generator. The tube was next surrounded with water at 80° , and a current of carbon dioxide conducted through it, when the green colored crystals sublimed. They were carefully collected and gave the results from which was deduced the formula given above. We have repeated the experiment of Piutti under

¹ *Annalen der Chemie*, 102, 115.

² *Annalen der Chemie*, 187, 255.

³ *G. ch. italiana*, 9, 538.

slightly modified conditions. Thus, we exposed 1.5 grams molybdenum trioxide and ten grams of phosphorus pentachloride in a sealed tube, filled with chlorine, to a temperature of 175°C . The sides of the tube, on cooling, were covered with greenish-black crystals. One end of the tube was broken open, quickly connected with a dry flask, after which the other end was opened and attached to a delivery tube in union with a chlorine generator. As the chlorine gas was conducted through the tube a gentle heat was applied to the latter, when a colorless liquid distilled over and was carefully collected. Later the greenish-black crystals sublimed and were collected separately in a dry vessel. The analysis of the colorless liquid just mentioned indicated it to be phosphorus oxychloride. The greenish-black solid was rapidly weighed out in weighing bottles. The vessel containing the portion intended for the chlorine determination was, after weighing, uncorked under water and the substance allowed to gradually enter the water. The disengaged gases were thus wholly absorbed.

Chlorine Determinations.—(1) 0.3702 gram substance gave 1.0881 gram silver chloride, equal to 0.2720 gram chlorine, or 73.47 per cent. (2) 0.3103 gram substance gave 0.9074 gram silver chloride, equal to 0.2268 gram chlorine, or 73.14 per cent.

Phosphorus Determinations.—(1) 0.5610 gram substance gave 0.1375 gram magnesium pyrophosphate, equivalent to 6.84 per cent. phosphorus. (2) 0.7991 gram substance gave 0.1914 gram magnesium pyrophosphate, equal to 6.67 per cent. phosphorus.

Molybdenum Determination.—The substance was digested with ammonium sulphide, and from this solution hydrochloric acid precipitated the trisulphide, which was changed to disulphide and weighed as such. 0.2385 gram material gave 0.0457 gram, equal to 19.17 per cent. Mo.

From these figures we deduce an atomic ratio, which would point to our compound as being a union of one molecule of molybdenum pentachloride with one molecule of the phosphorus haloid— $\text{MoCl}_5 \cdot \text{PCl}_5$. The theoretical percentages in this case are:

$\text{Mo} = 19.91$ per cent., $\text{Cl} = 73.65$ per cent., $\text{P} = 6.43$ per cent.

Our compound is greenish-black in color and decomposes

quite easily. The conditions under which we operated being slightly different from those of Piutti, it is not surprising that our product should be different. We used an excess of the phosphorus haloid and took care that the tube in which the reaction occurred contained chlorine gas. Subsequently we also distilled out the phosphorus oxychloride in a current of chlorine, and did not use carbon dioxide until after the removal of the liquid, and not while the tube was exposed to a gentle heat. The reaction which occurred with us may be, perhaps, represented as follows:



With even a larger excess of the phosphorus haloid the same product was found, so that it is hardly probable that we can hope to arrive at the hexachloride of molybdenum through this reaction.

UNIVERSITY OF PENNSYLVANIA,
April 26, 1894.

SEPARATION OF TITANIUM FROM IRON.

BY CHARLES BASKERVILLE.

Received April 16, 1894.

IN the recent literature which I have been able to consult, the separation of titanium from iron by means of sulphurous acid, has been confined to the sulphates of these two metals. This process is long and tedious and often unsatisfactory.

If a neutralized solution of titanium and iron chlorides, of not too great dilution, be boiled with an excess of sulphurous acid, the iron becomes deoxidized at once and a white flocculent precipitate of titanium settles out. By this means the titanium is obtained free from iron and requires no re-solution and second precipitation, as is frequently necessary for purification when precipitated from the sulphate. If the sulphate be changed into a chloride by precipitation with ammonium hydroxide and dissolving again in dilute hydrochloric acid and neutralizing the excess of acid with ammonium hydroxide, the separation is easily effected. The accuracy of the method is shown by the two following analyses:

| | Found. | Used. |
|------------------------|--------|--------|
| TiO ₂ | 0.0322 | 0.0308 |
| TiO ₂ | 0.0317 | 0.0314 |

The tedious boiling with sulphurous acid is avoided. A clean precipitate, which settles well and does not cling tenaciously to the sides and bottom of the beaker, filters rapidly and easily washed with hot water, is obtained. Salts of aluminum remain in solution.

UNIVERSITY OF NORTH CAROLINA.

NEW BOOKS.

THE TANNINS. A MONOGRAPH ON THE HISTORY, PREPARATION PROPERTIES, METHODS OF ESTIMATION AND USES OF THE VEGETABLE ASTRINGENT, WITH AN INDEX TO THE LITERATURE OF THE SUBJECT. BY HENRY TRIMBLE, Ph.M. Volume 2, pp. 172. Philadelphia: J. B. Lippincott & Co. 1894. Price, \$2.

The first volume of this work which appeared in 1892, was devoted to a general consideration of the subject and to gallo-tannic acid. The present volume deals primarily with the technically important tannins from the several species of oak bark and in a minor degree with those from mangrove, canaigre, and chestnut.

The tannins are usually dismissed by the chemist with the statement that they belong to a class of compounds about which very little is known and a few qualitative reactions at most, are given as characterizing them. Nevertheless they are of such importance that every one should know something of them. The author has endeavored to make an understanding of them possible by suggesting in some introductory remarks a method of study in which it is recommended to first investigate the sources of a tannin, then its history, method of preparation, properties, and finally a process for estimating it. It is usual for a chemist to begin with the last one of these; namely, the method of estimation and the result is invariably a failure.

With the exception of the historical chapters, this volume is made up almost entirely of the results of original research and the results of this work may best be understood by quoting from the final chapter, entitled Conclusions. "In looking over the composition of these tannins discussed in the volume, and comparing them with what appeared to be trustworthy results obtained in recent years by other investigators, we find that they

all arrange themselves according to their percentage of carbon and hydrogen into the following two groups :

| | I. The gallo-
tannin group. | II. The oak-
tannin group. |
|---------------|--------------------------------|-------------------------------|
| Carbon..... | 52.17 per cent. | 60.00 per cent. |
| Hydrogen..... | 3.10 " " | 5.00 " " " |

The tannins from nutgalls, chestnut wood and bark, pomegranate bark and sumac are classified under the first group, while those from oak bark, mangrove, canaigre, rhatany, kino, catechu, and tormentil, are found to fall within the limit of the second group.

This is nearly the old classification of "iron-blueing" and "iron-greening" tannins, but we believe with this important difference that oak-tannins so far as investigated give a green with salts of iron and not a blue as usually stated in the books. The blue color with salts of iron, the author claims, is obtained only with infusions of oak bark, and this is due to the presence of an iron-blueing coloring matter which accompanies the tannins.

S. P. S.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS. BY ARTHUR H. ELLIOTT, PH.D., published by the author. N. Y. 1894. Price \$2.00.

This treatise on qualitative analysis is neat in general appearance, printed in clear type and the nomenclature used is good. There is one feature of it; namely, the almost entire absence of equations representing the nature of reactions, which will bear criticism. It is impossible without a most elaborate system of experiments performed before the study of qualitative analysis is begun, to make students so familiar with the nature of chemical reactions, that these can be entirely neglected. Moreover, the average instructor of the subject prefers to keep the reactions constantly before the student as would be the case if they were introduced into the text.

It is easy to understand why such a treatise might be adopted by those engaged in the teaching of students of pharmacy and medicine, as the latter seldom enter deeply enough into the subject to consider the exact nature of the reactions involved. While leaving equations to be explained by the instructor

many minor points of manipulation are treated at unnecessary length. These might have been explained once for all beforehand.

A good feature is the mention of the occurrence in nature and in commerce of compounds of the element under discussion, a feature which is often ignored in books of its scope.

The chapters on the separations and detection of acids and bases are well written.

FRED'K W. SPANUTIUS.

"THERMODYNAMICS OF REVERSIBLE CYCLES IN GASES AND SATURATED VAPORS." BY M. I. PUPIN, PH.D.; edited by Max Osterberg. 114 pp. New York: John Wiley & Sons. 1894.

This little volume contains a "full synopsis of a ten weeks' undergraduate course of lectures," arranged (with the author's sanction) by a student of Columbia College. The course is designed as a theoretical introduction to a practical course in heat engines, not to a general course in physical chemistry. The Calculus is used throughout, but the mathematical notation is somewhat relieved by illustrations. The two laws are discussed successively with reference to perfect gases and Carnot's cycle. The integral and the differential equations of the indicator diagram are quite happily compared to Kepler's laws of planetary orbits as a whole, and Newton's successful analysis of these orbits into their minutest parts under the law of gravitation.

Steam is taken as the familiar type of saturated vapors; special emphasis is placed on the discussion of adiabatic and isothermal expansion; and reasons are given that the prevailing types of steam engines are not strictly reversible.

R. B. W.

SELECT TABLES FROM THE U. S. PHARMACOPŒIA, 1890. REPRINTED FOR READY REFERENCE IN DAILY PRACTICE. Published by the Committee of Revision. Philadelphia: Agents, P. Blakiston, Son and Company. 1893.

The list comprises: Alphabetical List of Volumetric Assays; Alcoholometric Table, according to E. R. Squibb; Saturation Tables; Equivalents of Weights and Measures, customary and metric; Table of Thermometric Equivalents; List of the Prin-

cial Pharmacopoeial Chemicals and Reagents, with their molecular weights; and Table of Atomic weights, according to L. Meyer and K. Seubert.

These respective tables are on 8vo. heavy paper for mounting on cardboard and hanging in the office or laboratory.

While the chemist may not use the whole Pharmacopoeia, these tables are just that part which will be found very useful to him. We cannot refrain from suggesting, however, that the practical chemist would make no mistake in familiarizing himself with the chemical portions of the whole book.

H. T.

NOTES.

Preparation of Standard Iodine Solutions.—The usual directions given for the preparation of standard solutions of iodine, to grind in a mortar, with a small quantity of water, the proper proportions of iodine and potassium iodide, transfer to the graduate-vessel and dilute, may be improved upon, both as to time required and danger of accidental loss of material, by the following method :

Iodine and potassium iodide, in the ratio of about two to three respectively, are carefully transferred to a graduate-flask and a weight of water added not greater than the weight of iodine used. The flask is then to be shaken until the scales of iodine disappear, care being taken not to splash the solution upon the stopper of the vessel. The required dilution is best made slowly with constant shaking. Three to five minutes are usually sufficient for the preparation of the solution and the rapidity and ease with which it may be accomplished largely depends upon using a minimum amount of water at first.

February 6, 1894.

DAVID HANCOCK.

Meeting of the Association of Official Agricultural Chemists.—The Executive Committee of the Association of Official Agricultural Chemists has decided to call the Annual Meeting of the Association for August 23, 24, and 25, 1894. The meetings will

be held in the Lecture Room of the National Museum, at Washington, D. C., beginning at 10 o'clock on Thursday, August 23.

The reporters for the meeting are as follows: Phosphoric acid—B. W. Kilgore, Raleigh, N. C. Nitrogen—J. M. Bartlett, Orono, Me. Potash—H. J. Wheeler, Kingston, R. I. Soils and ash—A. M. Peter, Lexington, Ky. Dairy products—F. H. Farrington, Champaign, Ill. Foods and feeding stuffs—H. J. Patterson, College Park, Md. Fermented liquors—Geo. F. Colby, Berkeley, Cal. Sugar—G. L. Spencer, Washington, D. C.

The co-operation of European chemists has been invited in the analytical work and several acceptances of the invitation have been received. It is urged upon all members who have communications to make to the Association to bring them properly prepared and ready for printing. Much delay has arisen heretofore in securing the manuscript promptly from the reporters and others presenting papers. The speedy publication of the proceedings will be greatly facilitated by bringing everything properly prepared.

H. W. WILEY, *Sec'y.*

The Assimilation of Free Nitrogen.—On page thirty of the January number of this JOURNAL I spoke of the activity of a germ which assimilated free nitrogen, attributing the discovery to Winogradsky and Warington. Mr. Warington writes me that he is not entitled to any credit for this discovery and on re-reading the original article in *The Chemical News* I find that he only called attention to its activity. The mistake arose from the intimate association in my mind of Mr. Warington's name with the researches into the nature of nitrifying organisms. I make this correction at the request of Mr. Warington.

H. W. Wiley.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

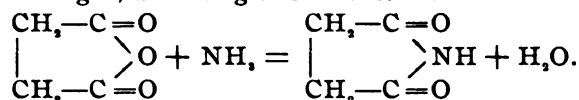
SUCCINIMID.

BY EDMUND H. MILLER.

PART I.

Received April 12, 1894.

SUCCINIMID was discovered in the year 1835 by Felix d' Arcet,¹ who prepared it by acting on succinic anhydride with ammonia gas, according to the reaction.



He noticed that when the two bodies were allowed to react, there was a great elevation of temperature, that a considerable amount of water was evolved, and that a compound much more fusible than succinic acid resulted; by aiding the reaction with heat, a white substance was sublimed which had none of the properties of succinic acid.

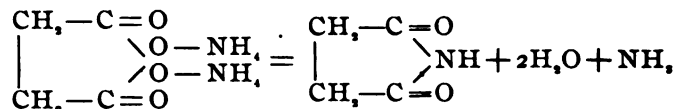
D' Arcet found that this substance which he called succinamid, crystallized in regular rhombs from ether and alcohol and contained one molecule of water when crystallized from that solvent, also it gave off ammonia when treated with hot caustic potash. He considered the formula as $\text{C}_4\text{H}_5\text{NO}$, from his analysis which would correspond to $\text{C}_4\text{H}_5\text{NO}$, according to the atomic weights now in use.

Bisuccinimid. This compound is identical with that prepared by D' Arcet and was so named by Fehling² who prepared it by conducting dry ammonia-gas over melted succinic acid, and recrystallizing the sublimate. He announced the melting point to be 210°C . Fehling also prepared this compound by

¹ *Ann. chim. phys.*, [2] 58, 282-300, 1835.

² *Ann. Chem.*, (Liebig), 49, 98, 1844.

neutralizing a solution of succinic acid with ammonia, evaporating to dryness, and then distilling; ammonia and water go off first and then bisuccinimid and a little succinic acid are sublimed.



Bisuccinimid was also obtained similarly from acid ammonium succinate by the splitting off of water.

Fehling found that an aqueous solution of bisuccinimid dissolved lead oxide in great quantities giving the lead salt containing fifty-eight per cent. of lead. He also announced that barium gave a similar compound.

The name succinimid was given to the compound by Laurent and Gerhardt¹ who devoted considerable time to its investigation, and first prepared the silver salt.

Trisuccinimid was prepared by Gerhardt and Chiozza² by the action of succinyl chloride on silver succinimid as follows: $\text{C}_4\text{H}_4(\text{CO})_2\text{Cl}_2 + 2\text{AgN}(\text{CO})_2\text{C}_4\text{H}_4 = \text{N}_3(\text{C}_4\text{H}_4\text{O}_2)_3 + 2\text{AgCl}$.

Teuchert,³ in his experiments on succinamic acid, gives the following statements concerning succinimid:

1. By treating succinimid with barium hydroxide the barium salt of succinamic acid is obtained.
2. On decomposing salts of succinamic acid by acids with the aid of heat, ammonium succinate is formed, not succinimid, as stated by Laurent and Gerhardt.
3. The compound called silver succinamate by Laurent and Gerhardt must not be considered as this compound, but as a silver hydroxide succinimid.

Teuchert also prepared the potassium, magnesium, manganese, cadmium, zinc, and copper salts of succinimid.

In 1869 Erlenmeyer⁴ redetermined the melting point of succinimid and found that instead of being 210° as stated by both Fehling and Teuchert, it was 125° – 126° . Erlenmeyer denied the

¹ *Compt. rend.*, 1847, 291, and 1849, 108.

² *Ann. Chem.*, (Liebig), 134, 136, 1865.

³ *Ann. Chem.*, (Liebig), 134, 136, 1865.

⁴ *Ztschr. für Chemie*, 12, 174, 1869.

conjecture made by Mendelejeff that succinimid might be identical with the isomeric compound, cyanpropionic acid on account of its formation from succinic anhydride, and from succinamid by the decomposition of two NH_2 groups into NH and NH_2 ; he ascribed its acid properties to the fact that the hydrogen is combined with a nitrogen attached to the rest of the molecule by two CO groups, and further states that it is an imid, and, therefore, plays the part of a monobasic acid.

Bunge,¹ in 1870, confirmed the melting point of succinimid obtained by Erlenmeyer; he found that it crystallized free from water when acetone was used as a solvent and obtained rhombic octahedra, whose axes were as follows: brachydiag.: makrodiag.: vertic. $a : b : c = 0.7888 : 1 : 1.3655$.

Bunge first replaced the hydrogen of the NH group by a non-metallic element when he formed iodine succinimid by treating silver succinimid with iodine dissolved in acetone or ether. The iodine succinimid reacted with silver nitrate and formed succinimid again. Menshutkin,² in 1872, found that there existed two silver compounds with succinimid, one containing no water of crystallization and the other one-half a molecule. He also states that the hydrogen of the NH group can be replaced by mercury, but that the lead, barium or calcium oxides convert it into the corresponding salt of succinamic acid, thus confirming Teuchert's results.

Succinimid may be converted into the amide by alcoholic ammonia at the temperature of the room, or more quickly by heating them together in a sealed tube at 100°C .

Menshutkin prepared succinimid by distilling succinic acid with acetamide. $\text{C}_4\text{H}_4\text{O}_4 + \text{C}_2\text{H}_5\text{ONH}_2 = \text{C}_4\text{H}_4\text{O}_4\text{NH} + \text{C}_2\text{H}_5\text{O} + \text{H}_2\text{O}$.

He also gave the following definition of an imid: "The imid is that acid amide, which, by the taking up of water, gives the amic acid, and by absorption of ammonia gives the amide." To Menshutkin³ belongs the distinction of first preparing an organic compound of succinimid; he accomplished this by distilling succinic acid and ethylamine and also by their solution in

¹ *Ann. Chem.*, (Liebig), Suppl., 7, 118, 1870.

² *Ann. Chem.*, (Liebig), 162, 166, 1872.

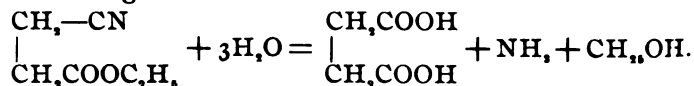
³ *Ann. Chem.*, (Liebig), 182, 90, 1876.

the proper proportions. Ethyl succinimid melts at 26° and boils at 234° , has a vapor density of 4.61 (compared to air) and is easily soluble in water, alcohol or ether. It is entirely decomposed into ethylamine and succinic acid by treating with caustic potash, and by gentle warming with barium hydroxide, gives the characteristic conversion into ethyl succinamic acid. Methyl succinimid, was similarly prepared.

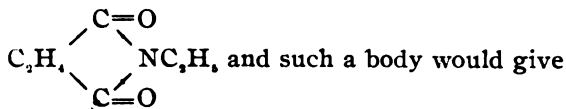
The first evidence of the symmetrical formula of succinimid is found in the statement of Bell¹ that succinimid by distillation with zinc dust, or on reducing its vapor by hydrogen, yields pyrrol; the presence of pyrrol is shown by the reaction with pine moistened with hydrochloric acid.

This fact is confirmed by Bernthsen² who repeated the experiments, and who also investigated the action of phosphorus trichloride on succinimid, and announced that it gave a fluid chloride. Erlenmeyer's statement that succinimid was not identical with cyanpropionic acid was confirmed in 1882 by Landsberg³ who, besides preparing a number of metallic salts of succinimid, found that ethyl succinimid when decomposed gave ethylamine and not ethyl alcohol. (This fact was first observed by Menshutkin, but he drew no conclusions from it.) Landsberg made the following statement of the matter:

If succinimid is $\text{C}_2\text{H}_4\text{—}\begin{smallmatrix} \text{—CN} \\ \text{—COOH} \end{smallmatrix}$ then the ethyl ester is $\text{C}_2\text{H}_4\text{—}\begin{smallmatrix} \text{—CN} \\ \text{—COOC}_2\text{H}_5 \end{smallmatrix}$; this body by treatment with either bases or acids would give



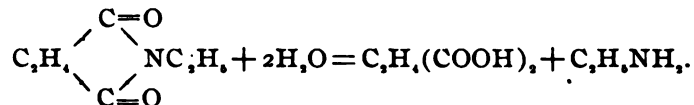
But if succinimid is $\text{C}_2\text{H}_4\text{—}\begin{array}{c} \text{C=O} \\ \diagup \quad \diagdown \\ \text{NH} \end{array}$ the ethyl ester is



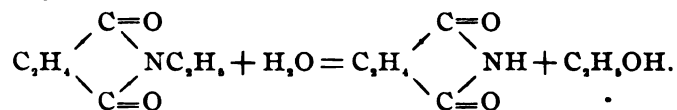
¹ *Ber. d. chem. Ges.*, 13, 877, 1880.

² *Ber. d. chem. Ges.*, 13, 1047, 1880.

³ *Ann. Chem.*, (Liebig), 215, 172, 1882.

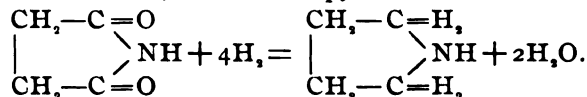


The fact that Menshutkin obtained succinimid and alcohol when he treated silver succinimid with ethyl iodide instead of ethyl succinimid and silver iodide, is explained by the water of crystallization present in some silver succinimid which decomposes the ethyl ester of succinimid first formed as follows:



Cimian and Silber¹ investigated the action of bromine on succinimid. They found that the hydrogen of the imid group was not attacked but that when a calculated amount of bromine was dropped into a flask containing succinimid heated to 160° C., that hydrobromic acid was given off, and bibrommaleicimid (CBr)₂(CO)₂NH was formed (M. P. 225° C). This imid when treated with aqueous caustic potash gave bibrommaleic acid. The corresponding anhydride, and the barium and silver results were also made. Bender² treated succinimid with calcium chloride in acetic-acid solution and obtained chlorine succinimid C₂H₄(CO)₂NC₂H₅, which crystallizes in large colorless crystals from boiling benzene, melts at 148° C. without decomposition, and by treatment with hydrochloric acid or alkalis forms succinimid again.

Ladenburg³ found that by reducing succinimid by sodium, in an alcoholic solution, he obtained pyrrolidin.



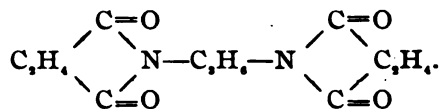
A curious body was made by Strache⁴ by heating together two molecules of succinic anhydride and one of propylene diamine, called propylene succinimid. Its melting point is 98°-100° C. and has the formula

¹ Ber. d. chem. Ges., 17, 556, 1884.

² Ber. d. chem. Ges., 19, 2273, 1886.

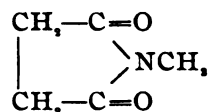
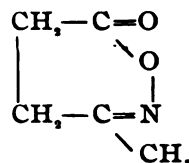
³ Ber. d. chem. Ges., 20, 215, 1887.

⁴ Ber. d. chem. Ges., 21, 2360, 1888.



A most extraordinary method of making methyl succinimid was announced by Bredt and Boeddinghous¹ in 1889. They found that the valeroximidolacton of Rischbieth, which is made by treating isonitrosovalerianic acid (made from levulinic acid and hydroxylamine) with concentrated sulphuric acid, to be identical with methyl succinimid, both in melting and boiling points and to give succinic acid and methylamine on treatment with caustic potash.

Methyl Succinimid.

 γ valeroximidolacton.

The only conclusions that can be drawn from this remarkable reaction are that either the formula given above for methyl succinimid is wrong or, as is more probable, that the compound must undergo an elaborate molecular rearrangement.

The substitution of a bromine in one of the CH_3 groups of succinimid, was accomplished by Kusserow² in 1889. He formed bromsuccinimid $\text{C}_2\text{H}_4\text{Br}(\text{CO})_2\text{NH}$ by heating water-free succinimid and bromine dissolved in chloroform in a sealed tube at 120° – 130° C. After heating for two or three hours the bromine disappears and the substitution product is seen as a brown oil under the chloroform. $\text{C}_2\text{H}_4(\text{CO})_2\text{NH} + 2\text{Br} = \text{C}_2\text{H}_4\text{Br}(\text{CO})_2\text{NH} + \text{HBr}$.

If water is present and the tube is heated to 160° a mass of white crystals results and scarcely any pressure. The bromsuccinimid is attacked by the hydrobromic acid and water as follows:



Anilidosuccinimid, $\text{C}_2\text{H}_4(\text{NH} \cdot \text{C}_6\text{H}_5)(\text{CO})_2\text{NH}$, is formed by warming monobromsuccinimid with an excess of anilin on the

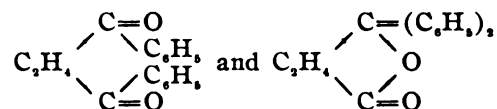
¹ *Ann. Chem.*, (Liebig), 251, 316, 1889.

² *Ann. Chem.*, (Liebig), 252, 158, 1889.

water-bath; from this the following compounds have been made: nitrosoanilidosuccinimid $C_6H_5(N-NOC_6H_5)(CO)_2NH$ and acetylanilidosuccinimid $C_6H_5(NC_6H_5OC_6H_5)(CO)_2NH$.

Anilido succinanil $C_6H_5(NHC_6H_5)(CO)_2NC_6H_5$ is formed by warming monobromsuccinic acid with an excess of anilin and recrystallizing the product from alcohol. The corresponding nitroso-compound and the amic acid have also been prepared.

The only investigation pointing towards the existence of an unsymmetrical as well as a symmetrical succinimid is that of Auger.¹ He succeeded in preparing two succinimids by the reaction of ammonia on succinyl chloride in the proportion of eight of the unsymmetrical to one hundred of the symmetrical. He also formed the silver salt corresponding to the silver salt of symmetrical succinimid, but failed to make the unsymmetrical succinimid. Auger's investigation on the imid is very incomplete so that to draw any inference as to the molecular arrangement of succinimid, we must consider his work on succinyl chloride and phtalimid. Succinyl chloride when acted on by benzene and aluminum chloride in the cold for five hours, gives a mixture of a symmetrical and unsymmetrical compound.



The unsymmetrical compound melts at 90°C ., is insoluble in water and cold alkalies, and has a neutral reaction. When treated with potash on the water-bath and then made acid with hydrochloric

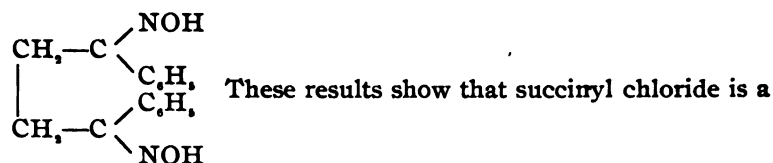
acid γ diphenyloxbutyric acid separated out, C_6H_5

$$\begin{array}{c}
 \text{C}=(\text{C}_6\text{H}_5)_2 \\
 \diagup \quad \diagdown \\
 \text{C}_6\text{H}_5 \quad \text{OH} \\
 \diagdown \quad \diagup \\
 \text{COOH}
 \end{array}$$

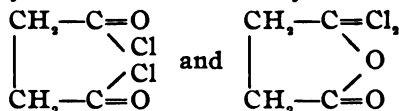
as we would expect from the lactone formula, this body melts at 145° and gives water and the unsymmetrical lactone, M. P. 90°C .

The symmetrical body, separated from the unsymmetrical by fractional distillation, is formed in much smaller quantity. It melts at 134°C . and is unacted on by alkalies. Its symmetrical constitution is shown by the formation of a dioxime.

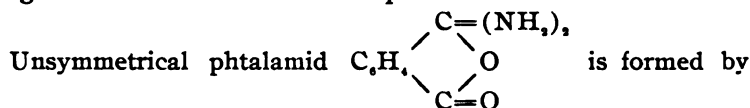
¹ *Ann. chim. phys.*, [6] 22, 289-368, 1891.



mixture of the symmetrical and the unsymmetrical.

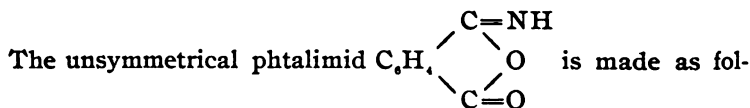
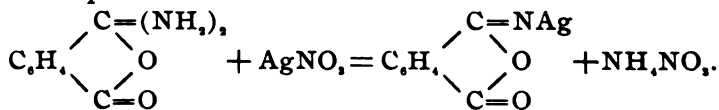


If there are two succinyl chlorides, it would seem that there should be two succinimids and the probability of the existence of the unsymmetrical, at present unknown, is more evident by Auger's research on the amids of phthalic acid.



dropping phtalyl chloride into a large excess of aqueous ammonia, then evaporating, drying, and extracting with ninety-nine per cent. alcohol and recrystallizing. It begins to melt at 90°C . and is soluble in water while the symmetrical phtalamid is not.

The unsymmetrical compound gives a silver salt having the composition $\text{C}_6\text{H}_4\text{O}_2\text{NAg}$ which is the silver salt of the unsymmetrical phtalimid.



lows: To a seven per cent. aqueous solution of the unsymmetrical phtalamid add, in the cold, a quantity of hydrochloric acid calculated to remove one NH_2 . A voluminous white precipitate is the immediate result, which, when recrystallized from ninety-five per cent. alcohol, gives a compound which has the same percentage composition as phtalimid, the same appearance,

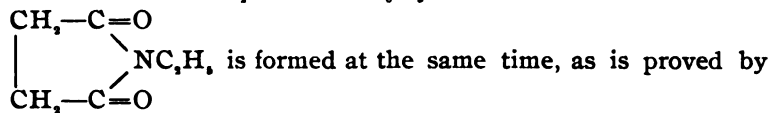
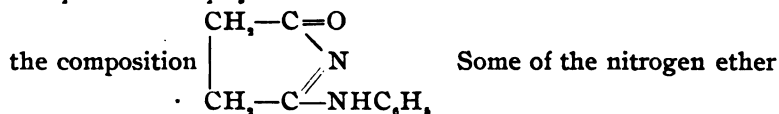
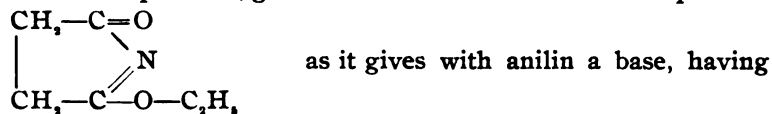
the same solubility in water, the same acid reaction, and if heated very gently, has the same melting point. But if it is heated rapidly, to about 145°C ., it melts, giving a perfectly limpid liquid which in about half a minute, without the disengagement of any gas or vapor, solidifies completely and does not melt till 228°C . is reached, the melting point of the symmetrical phtalimid. It therefore seems that on heating it has undergone a molecular rearrangement and has been converted into the more stable sym-



The unsymmetrical phtalimid, though similar to the symmetrical in most of its properties, is more easily decomposed by water giving first the amic acid and then the ammonium salt.

The oxygen ethers of succinimid isomeric with the nitrogen ethers previously described, have been prepared recently by Comstock and Wheeler,¹ as follows:

Oxygen ethyl-succinimid. Dry silver succinimid was allowed to stand for several weeks at the ordinary temperature with one molecule of ethyl iodide, diluted with three times its weight of dry chloroform; a dark oily residue was obtained which, when distilled under diminished pressure, gave the ether. It must have the composition



allowing the mixture to stand for some time with water, which converts the oxygen ether into succinimid, and then distilling with caustic potash; the distillate showed the presence of primary amine by the isonitril reaction.

¹ *Am. Chem. J.*, 13, 520, 1891.

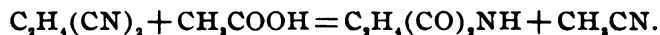
The nitrogen ether so obtained agrees in properties with that described by Menshutkin. Oxygen propyl-succinimid was made in the same way, also the isomeric nitrogen ether. The oxygen propyl ether as well as the ethyl ether gives with anilin the base $C_{10}H_{10}N_2O$, melting point $216^{\circ}C$.

Succinimid bromide has been made by Lengfeld and Steiglitz¹ by adding bromine to a solution of succinimid in sodium hydroxide cooled by ice; the yield is ninety to ninety-five per cent. of the theoretical. The melting point is 172.5° ; acids instantly liberate bromine and regenerate succinimid; water decomposes it slowly; when pure and dry, it is stable. It is evidently analogous to the succinimid iodide of Bunge, and the succinimid chloride of Bender.

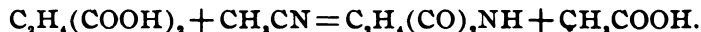
The above compound sometimes called bromyl succinimid was made in the same year by Seliwanow² from succinimid and bromyl-acetamide; he gives its melting point as 161° – 162° and states that it can also be made from succinimid and hypobromous acid; in the presence of water it acts like hypobromous acid, as does the corresponding chlorine compound. He regards the compound as an amide of hypobromous acid.

It only remains for me to describe here briefly, three new methods by which I have made succinimid.

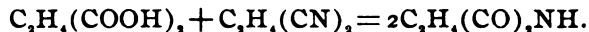
No. 1. On heating together ethylene cyanide and acetic acid in a sealed tube for eight hours at a temperature of 180° – $200^{\circ}C$. the following reaction takes place:



No. 2. On heating under the same conditions succinic acid and acetonitril, succinimid is formed as follows:



No. 3. On heating in the same way equal molecules of succinic acid and ethylene cyanide, two molecules of succinimid are formed, the yield being nearly theoretical.



¹ *Am. Chem. J.*, 15, 215, 1893.

² *Ber. d. chem. Ges.*, 25, 3623, 1892, and *Ber. d. chem. Ges.*, 26, 423, 1893.

●
PART II.

MY EXPERIMENTS ON SUCCINIMID.

First Method. Ethylene Cyanide and Acetic Acid.—Tube No. 1. Three grams of ethylene cyanide (one molecule) were dissolved in 2.25 grams of glacial acetic acid (one molecule) in a small thick glass tube, then a few drops of acetic anhydride were added to render the acid anhydrous; the tube was sealed and heated for two hours at 120° – 130° C. and then as no change seemed to have taken place, for six hours at 200° C. On cooling, the tube contained a thick brown liquid.

When this tube was opened several months later, some pressure was observed but no colored flame; the contents were transferred to an evaporating dish and allowed to evaporate slowly. Crystals soon made their appearance, and the entire mass finally turned solid and smelled strongly of acetic acid. To determine a method of purification the solubility of the product was tested as follows:

| Cold. | Hot. |
|---|--------------|
| Ether, partially soluble | same |
| Chloroform, partially soluble..... | same |
| Ethyl alcohol, soluble..... | very soluble |
| Methyl alcohol, very soluble..... | very soluble |
| Benzene, slightly soluble | soluble |
| Amyl acetate, slightly soluble..... | same |
| Carbon disulphide, readily soluble..... | same |
| Water, very soluble | same |

The mass was dried and extracted with dry ether in a continuous extractor for several hours. On allowing the ether extract to cool, diamond-shaped crystals formed, which were removed and their melting point found to be 123° – 124° C. (uncorrected). The ether solution was evaporated to dryness and recrystallized from methyl alcohol, giving white crystals melting at 122.5° – 123° C.

These crystals were tested for nitrogen by the prussian-blue reaction, which showed that it was present without doubt. They were also tested with methyl orange in aqueous solution and gave a very light pink, showing that it was neither strongly acid nor alkaline. Comparative tests were made with both cyan-acetic acid and succinimid, and the color was found to be almost identical with the latter.

Combustions for carbon, hydrogen and nitrogen were made on some of the best crystals as follows: Nitrogen combustion: weight of substance 0.1211 gram gave 15.15 cc. of nitrogen at a temperature of 23.5°, barometer 769.5 mm.; 14.23 per cent. Carbon and hydrogen determination: weight of substance, 0.1509 gram; weight CO₂, 0.2554; weight H₂O, 0.0760, equivalent to 45.98 per cent. carbon and 5.59 per cent. hydrogen.

As the amount of the recrystallized substance was very small, these combustions could not be checked but some more of the substance had to be prepared as is described later.

Tube No. 2 contained three grams of ethylene cyanide, 4.5 grams of glacial acetic acid and a few drops of acetic anhydride, or one molecule of the cyanide to two of the acid. This tube was treated exactly like No. 1, and the only noticeable difference was that its contents, on evaporation, smelled more strongly of acetic acid, and required longer heating before they solidified, owing to the presence of the greater excess of acetic acid.

The melting point of the crystals from this tube, when purified by crystallization from methyl alcohol, was found to be 123° C. (uncorrected).

A nitrogen determination on crystals from tube No. 2 gave the following figures: Weight substance, 0.2026 gram; volume of nitrogen, 25.5 cc. at 22° C., and 772.5 mm., 14.44 per cent.

The carbon and hydrogen were determined as follows: Weight substance, 0.3303 gram; weight CO₂, 0.5857 gram; weight H₂O, 0.16055 gram, equivalent to carbon 48.36 per cent., and hydrogen 5.39 per cent.

I considered that this substance was identical with that obtained from tube No. 1 and that it was probably succinimid.

The following table shows a comparison of my first results with the calculated percentage of succinimid:

| | Tube No. 1. | Tube No. 2. | Succinimid. |
|------------|----------------|----------------|---------------------------------------|
| C..... | 45.98 | 48.36 | 48.48 |
| H..... | 5.59 | 5.39 | 5.05 |
| N..... | 14.23 | 14.44 | 14.14 |
| M. P. | 123°—124° | 123° | 124°—125° |
| | (uncorrected.) | (uncorrected.) | (according to different authorities.) |

As the yield from tube No. 2 was slightly larger than from

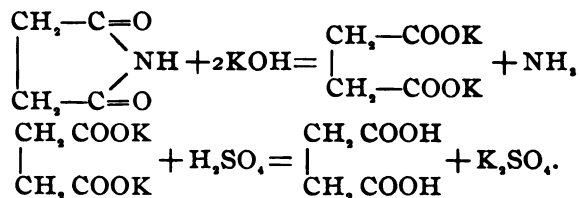
tube No. 1, some more of the substance was made for further investigation by using two molecules of acetic acid to one of ethylene cyanide.

Tube No. 3 contained ethylene cyanide, twelve grams, acetic acid, sixteen grams, acetic anhydride, five drops, and was heated for three hours at 170°–180° C. and then for six hours at about 200° C. The appearance of the tube on cooling was the same as Nos. 1 and 2.

Thinking that, if succinimid was produced, acetonitril must also be formed, an endeavor was made to separate by distillation the more volatile contents of the tube before transferring them to an evaporating dish; and by using a paraffin bath, a few cubic centimeters of a liquid which smelled of acetic acid and acetonitril, were obtained.

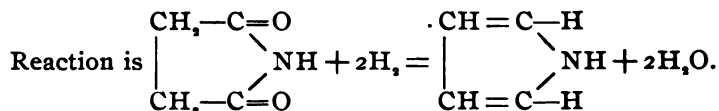
The contents of tube No. 3, after evaporating, were extracted with dry ether for five hours and yielded twelve grams of good dry crystals (theory, 14.85 grams). A portion of these crystals was purified by crystallization from methyl alcohol and combustions were made on it as follows: Nitrogen determination: Weight substance, 0.1923 gram; volume of nitrogen, 24.6 cc.; temperature, 25° C.; pressure, 771 mm.; 14.34 per cent. nitrogen. Carbon and hydrogen determination: Weight substance, 0.2948 gram; weight CO₂, 0.5264 gram; weight H₂O, 0.1416 gram; 48.69 per cent. carbon; 5.33 per cent. hydrogen.

These figures agree closely with the percentage composition of succinimid, but to confirm them some of the crystals were treated with boiling aqueous caustic potash; ammonia was given off and succinic acid was formed, which was obtained by extracting with ether, and its melting point determined. This agreed with the established melting point of succinic acid. The reactions are as follows:



Another portion of the pure crystals was tested for reduction

to pyrrol as follows: A small portion of the crystals was ground fine with zinc dust in an agate mortar, and the mixture then transferred to a very small distilling flask and heated over a Bunsen burner; the distillate was but a few drops, but the fumes turned a piece of pine moistened with hydrochloric acid bright red, showing unmistakably the presence of pyrrol.



Some of the crystals obtained from tubes 1, 2, and 3 are large and diamond-shaped when crystallized from ether and retain this characteristic diamond form even when recrystallized from methyl alcohol.

The lack of agreement in the melting points of succinimid and my crystals is explained by the length of the column of mercury outside the liquid in which the melting point was determined. The correction for this was found to be 1.8° , which would make my results agree with the accepted melting point of succinimid. To make sure that there was no mistake in this determination the melting point of some succinimid, made by the distillation of ammonium succinate, was found by my thermometer under the same conditions as obtained in the previous determination, to be 123°C .

Second Method. Acetonitril and Succinic Acid.—This method was tried to see whether the position of the COOH and CN groups had any effect on the reaction.

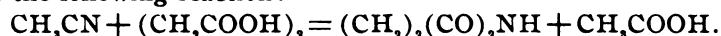
Tube No. 4. Succinic acid, 17.7 grams (one molecule), acetonitril, 12.3 grams (two molecules), and acetic anhydride four drops, were heating in a sealed tube for eight hours as described under tube No. 3. On cooling, this tube contained a black liquid but not as thick as the preceding. The contents were evaporated and extracted as before. Crystals were obtained which melted at 123° but were not entirely diamond-shaped. The yield in this case was nine grams but would probably have been larger had the tube been heated longer.

The pure crystals from this tube were treated with hot KOH and gave ammonia and succinic acid which was identified by its

melting point. They also gave pyrrol when distilled with zinc dust as in the previous case. Combustions for carbon, hydrogen and nitrogen were made with the following results:

Carbon and hydrogen: Weight substance, 0.2857 gram; weight CO_2 , 0.5080; weight H_2O , 0.1382; equivalent to carbon, 48.49 per cent.; hydrogen, 5.37 per cent. Nitrogen: weight substance, 0.2787 gram; volume of nitrogen, 36.45 cc. at 27°C . and 766 mm.; pressure, equivalent to 14.54 per cent. nitrogen. (This figure is too high as NaOH was used to absorb the CO_2 , because the KOH had given out.)

The crystals from this tube are undoubtedly identical with those obtained from Nos. 1, 2, and 3, and are formed according to the following reaction:

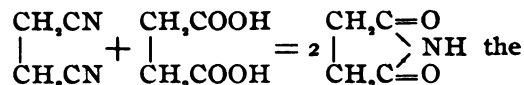


The second molecule of acetonitril plays no part in the reaction but was used to make the experiment as far as possible the reverse of No. 3.

I had hoped that these experiments might throw some light on the molecular arrangement of succinimid, but think they have not. Though the succinimid produced is undoubtedly identical with that formed by the distillation of ammonium succinate, and is probably symmetrical on account of its reduction to pyrrol, and is formed invariably to whichever radical the cyanogen group is attached, still I think, considering the analogy of phthalimid, that if an unsymmetrical succinimid were produced at first, that under the conditions of heat and pressure it would be converted into the more stable symmetrical compound.

Third Method. Ethylene Cyanide and Succinic Acid.—Tube No. 5 contained ethylene cyanide, eight grams, (one molecule); succinic acid, 11.8 grams, (one molecule); acetic anhydride, two drops. This tube was heated for six hours at a temperature of about 200°C . On opening, considerable pressure was observed and the contents were solid and semi-crystalline. The hard mass was extracted with ether as before; the crystals were partly diamond-shaped and partly rhombic octahedra; some had flat, diamond-shaped bases, and a pyramid on top, showing that the diamond-shaped crystals were but modifications of the rhombic octahedra, the ordinary crystalline form of succinimid.

According to the reaction



theoretical yield would be 19.8 grams. 16.2 grams, or 81.8 per cent. of the theoretical were obtained. The residue of carbon weighed 1.7 grams, which would be equivalent to 3.5 grams of succinimid, so that the loss due to manipulation was only 0.1 gram.

Two determinations of the melting point of the succinimid from this tube gave 122° C., or corrected, 123.8° C. The crystals also gave on distillation with zinc dust, pyrrol as before. Prof. Moses, of the School of Mines, very kindly measured the crystals obtained. The results were as follows:

$$a : b : c = 0.8044 : 1 : 1.471.$$

Some allowances must be made on account of the hollow faces of these crystals in comparing these figures with those of Bunge:¹

$$a : b : c = 0.7888 : 1 : 1.3655.$$

Molecular Weight Determinations.—In order to determine that the molecular weight of succinimid was not a multiple of that ascribed to it (99), it was determined by Raoult's method, using water and glacial acetic acid as solvents. The method pursued was that given in Wiedermann and Ebert's *Physikalisches Praktikum*, Braunschweig, 1890.

First determination. In this experiment water was used as a solvent; the freezing mixture was snow and hydrochloric acid; the substance used was made by the action of acetonitril on succinic acid (tube No. 4).

The thermometer was set for water by changing the amount of mercury in the column, and then the freezing point of distilled water was determined twice. Both determinations gave 2.40 on the Beckman thermometer. 8.0449 grams of water were used which filled the portion of the tube in the freezing mixture; after the second determination the ice was allowed to melt and 0.1146 grams of the substance introduced through the side tube; when this had dissolved completely, which required an hour and a half, the mixture was again chilled; the mercury went down gradually to 0.8° and then rose rapidly to 2.12° where it remained

¹ *Ann. Chem.*, (Leibig), Suppl., 7, 118, 1870.

stationary for some time; after making sure that this was the correct reading, the mixture was allowed to melt and a second addition of 0.1153 gram of substance introduced as before. The process was repeated and the freezing point found to be 1.84° ; using for water the value 18.5, the calculation is as follows:

$M = \frac{I}{e}$ or M , the molecular weight, is equal to the constant determined for water by use of known substances divided by e the depression in degrees centigrade produced by one gram of the substance dissolved in 100 grams of water. To obtain e we have the following proportions for the first addition:

$$0.1146 : 8.0449 :: X : 100.$$

X , number of grams per hundred grams of solvent in the solution used, 1.424.

$$1.4245 : 1 :: 0.28 : e \quad e = 0.1965^{\circ}$$

Substituting in formula $M = \frac{I}{e} = \frac{18.5}{0.1965}$ or $M = 94.1$. For the second addition:

$$\begin{array}{ll} 0.2299 : 8.0449 :: X : 100 & X = 2.8577 \\ 2.8577 : 1 :: 0.56 : e & e = 0.1959^{\circ} \quad M = 94.4 \end{array}$$

Though the results were sufficiently accurate to show that the formula of succinimid was not a multiple of ninety-nine, further experiments were made to confirm them and to obtain results with some other solvent as a check.

Benzene was tried but though a much smaller amount of substance was used, it was not sufficiently soluble to give any satisfactory results. On chilling the mixture, the succinimid gradually separated out and the thermometer did not go down regularly below the freezing point and then rise to and remain at a definite place, but went down continually by jerks. In determining the freezing point of benzene, snow and a little salt was used and it was found inadvisable to have the freezing mixture more than 10° below the freezing point of the solvent.

Ethylene bromide was next tried but exactly the same difficulty was encountered as with benzene. Water was again used as a solvent and the following figures were obtained with crystals from tube No. 3.

Weight of solvent, 9.6352; freezing point, 4.72° .

First addition: Weight substance, 0.0536; freezing point, 4.626° ; $e=0.1689$; $M=109.4$.

Second addition: Weight substance, $0.0536 + 0.0568 = 0.1104$; freezing point, 4.55° ; $e=0.1485$; $M=124.6$.

Third addition: Weight substance, $0.0536 + 0.0568 + 0.0586 = 0.1690$; freezing point, 4.395° ; $e=0.1853$; $M=99.8$.

Fourth addition: Weight substance, 0.2224; freezing point, 4.22° ; $e=0.2168$; $M=85.3$.

Determinations Using Acetic Acid.—99.5 per cent. acetic acid was used in this work and the figure 38.6 (taken from Ostwald on Solution, page 229) was employed. A new difficulty was encountered in these determinations, which was that the acetic acid froze at a lower temperature each time; successive determinations gave the following figures: 2.17° , 2.13° , 2.105° , 2.08° . The explanation of this is that the acetic acid is constantly becoming weaker and the greater proportion of water gives a lower freezing point. In making the determination it was therefore necessary to estimate the probable depression due to evaporation and subtract it from that observed.

The determination was made substantially as before except that cold water was used instead of the freezing mixture. As the lowering of the freezing point of the acetic acid seemed to grow slightly less on successive freezings, the probable freezing points for the next three determinations were estimated at 2.055° , 2.035° , and 2.015° , respectively. Weight of acetic acid, 12.1795 grams; weight of substance (succinimid from tube No. 3), 0.0700.

Second determination on first addition: Freezing point 1.81° ; $e=0.3893$; $M=99.1$. Second addition: Weight solvent, 12.1795 grams; weight of substance, $0.0700 + 0.0965 = 0.1665$; freezing point, 1.50° ; depression, 0.515; $e=0.3840$; $M=100.5$.

The average of two determinations on substance from tube No. 4 is 94.25, using water as the solvent.

The average of four determinations on substance from tube No. 3 is 104.8 (solvent water).

The average of two determinations on same, using acetic acid as the solvent, is 99.8.

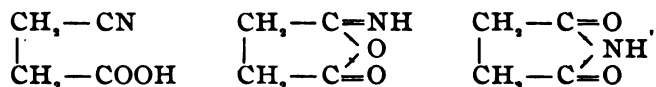
General average, 99.61.

Conclusions.—Succinimid has been made as follows:

1. By the action of ammonia on succinic anhydride. (D'Arcet.)
2. By passing ammonia over melted succinic acid. (Fehling.)
3. By the distillation of ammonium succinate. (Fehling.)
4. By the distillation of acid ammonium succinate. (Fehling.)
5. By the distillation of succinic acid and acetamide. (Menschutkin.)
6. By heating ethylene cyanide and acetic acid in a sealed tube.
7. By heating in the same way acetonitril and succinic acid.
8. By heating, as above, ethylene cyanide and succinic acid.
9. Methyl succinimid has been made by the action of sulphuric acid on isonitrosovalerianic acid.

There seems to be no doubt that the succinimid produced by all these methods is identical. Its molecular weight and percentage composition show that the formula must be $C_4H_5NO_2$.

For its molecular arrangement, we have to choose between the following graphic formulae:



The first is inadmissible as it is shown by Landsberg that the ethyl ether on decomposition gives ethylamine, while the ethyl ether of β cyanpropionic acid would give ethyl alcohol; it also seems to me that β cyanpropionic acid would turn methyl-orange pink as cyanacetic acid does, but as succinimid does not.

Between the last two, the facts that succinimid on reduction with zinc dust gives pyrrol and with alcohol and sodium pyrrolidin and that succinimid is formed invariably to whichever radicle the CN and COOH groups are attached, are the most important evidences in favor of the symmetrical arrangement. We would also expect that the symmetrical would be the more stable compound. This is borne out by the well-known stability of succinimid, which can be distilled without decomposition.

I believe that succinimid is symmetrical as all the facts observed point to that conclusion; but I think it cannot be proved absolutely until its specific refractive power is determined, which will show in connection with the specific refractive powers of the other elements and with that of nitrogen when

joined in different ways, whether, in the case of succinimid, it is attached to one or two carbon atoms.

If β cyanpropionic acid could be isolated, it might on heating be converted into the isomeric unsymmetrical succinimid, and it was with a view to this that the attempts to make this acid, described in part third, were undertaken.

PART III.

ATTEMPTS TO MAKE AND ISOLATE β CYANPROPIONIC ACID
BY THE ACTION OF POTASSIUM CYANIDE ON
 β IODOPROPIONIC ACID.

No. 1. Seventy-five grams of β iodopropionic acid were dissolved in ninety cc. of hot water and neutralized with thirty-four grams of potassium carbonate, then thirty-five grams of finely pulverized potassium cyanide were added and the solution stirred till it dissolved. It was next evaporated and stirred continuously with a thermometer till the temperature reached 132° C. During this time some hydrocyanic acid was given off; the mass was dissolved in a little hot water and neutralized with hydrochloric acid, then evaporated on a water-bath to a syrupy mass and shaken with ether. The ether extract on evaporation yielded nothing.

Before the experiment could be repeated, it was necessary for a new supply of β iodopropionic acid to be made from glyceric acid, and as no phosphorous di-iodide was to be obtained, that had to be prepared also.

After having secured a supply of the iodo acid, the attempts to convert it into the cyan acid were resumed.

No. 2. Fifty grams of β iodopropionic acid were dissolved in a little hot water and 22.8 grams of finely pulverized potassium carbonate added and the carbonic acid boiled out; 21.66 grams of potassium cyanide were dissolved in as little hot water as possible and added to the solution now containing the potassium salt of β iodopropionic acid. The solution was allowed to stand over night and then boiled with a return condenser for five

hours, in an endeavor to ensure the formation of KI and cyanpropionic acid. The liquid was then put in an evaporating dish and neutralized with a calculated quantity of normal sulphuric acid and shaken with ether many times, the ether being recovered and used repeatedly, the residues from which the ether was distilled, were dissolved in water and shaken with lead carbonate separately. This gave an effervescence showing the formation of the lead salt of an acid and also of some lead sulphate. These several mixtures were each filtered and then saturated with hydrogen sulphide to precipitate the lead and set free the cyan acid. The lead sulphide was filtered out and the solution evaporated as far as possible on a water-bath. It was then put in a desiccator under diminished pressure over sulphuric acid and left for twenty-four hours. At the end of that time needle-like crystals appeared; they were left there for several days longer and the crystals were subsequently removed and dried between filter paper.

The crystals were white and small and not over 0.100 gram in weight. This method seemed an improvement over the use of hydrochloric acid but the yield was so extremely small as to be rather discouraging.

No. 3. Twenty-five grams of β iodopropionic acid were dissolved in hot water and potassium carbonate added until the solution was alkaline. It was then warmed on a water-bath till the effervescence ceased when nine grams of freshly pulverized potassium cyanide were added and the mixture heated till it was dissolved. In this way the amount of water present was reduced to a minimum. It was evaporated to a syrup on a water-bath and heated over a flame until the temperature reached 125° C. It was next transferred to a beaker and made acid by the addition of three cc. of concentrated sulphuric acid previously diluted with water. Carbon dioxide was given off as before. It was then shaken with large quantities of ether to extract the free acid and let stand for four weeks before the ether was distilled off. The residue was similar to that obtained by No. 2, but the quantity was very small.

No. 4. Twenty-five grams of β iodopropionic acid were dissolved in hot water and potassium carbonate was added until the

reaction was alkaline, which required 19.75 grams owing to the poor quality of the iodo acid used. 11.4 grams of finely ground potassium cyanide were added and the solution warmed till it dissolved. The solution was at this time straw colored and was heated to boiling and boiled for about a minute, when it became dark reddish brown and smelled of hydrocyanic acid. The heating was stopped here, as the destruction of the compound by overheating was feared.

8.12 cc. of concentrated sulphuric acid diluted with thirty cc. of water were added which gave a lively effervescence of hydrocyanic acid. It was evaporated carefully over a flame and the sticky mass put in a continuous extractor and extracted for several hours. The ether was finally evaporated and the yellowish crystalline residue was dissolved in methyl alcohol which was put aside to crystallize. From this lot were obtained 0.200 gram of good crystals.

No. 5. The same method was tried again but the mass was heated to 135° instead of 125° and the acid was not added until after the evaporation. Twenty-five grams of β iodopropionic acid of good quality were dissolved in twenty-five cc. of hot water and neutralized with 10.15 grams of finely pulverized potassium carbonate; after it was warmed to drive out carbon dioxide, 11.35 grams of ground potassium cyanide were added. The mixture was placed on the water-bath to react for three hours. It was then heated over a flame until the temperature reached 135° after which it was allowed to cool and 4.17 cc. of concentrated sulphuric acid diluted with fifteen cc. of water were added. There was some smell of hydrocyanic acid but not so much as in No. 4. This was next evaporated rapidly over a flame till the mass was only slightly sticky, transferred to an extractor and extracted with ether for four hours. The residue was tested and found to be potassium cyanide and iodide. The ether solution was distilled and the residue recrystallized from methyl alcohol as before. The yield was small as usual.

No. 6. The effect of pressure as well as heat was tried in this and the following experiment :

Two lots of ten grams each of β iodopropionic acid were weighed out and mixed with 3.46 grams of fine potassium car-

bonate. To this, water was added and the whole warmed until it dissolved. Then 3.28 grams of potassium cyanide were dissolved in water and added to each, and the resulting solutions put in tubes. On standing, the solutions became dark colored; they were sealed and heated for three hours at 112°C ., then allowed to cool. A black film appeared on the inside of the tubes similar to that deposited on the flask when boiled with a return condenser. They were heated three hours longer at the same temperature and examined; the contents seemed to be turning solid. The tubes were heated again for seven hours and when opened there was no perceptible pressure.

The contents of the two tubes were combined and evaporated on a water-bath to a syrup and enough sulphuric acid added to neutralize all the potassium carbonate. There was no effervescence whatever which was encouraging as it indicated that the potassium cyanide had been converted into iodide. It was replaced on the water-bath to evaporate, and when dry, extracted in a continuous extractor for six hours. The ether was then distilled and the residue of nearly white needle-shaped crystals dissolved in methyl alcohol and set aside to crystallize. After four days the crystals were dried and their melting point was found to be 165° . The yield was 0.658 gram; theory, 5.1.

No. 7. This experiment differs from the preceding in that two molecules of potassium cyanide were used instead of potassium carbonate; one to form the potassium salt of the acid and the other to furnish the CN group.

Two portions of five grams each of β iodopropionic acid were weighed out, and to them were added 3.28 grams of potassium cyanide, dissolved in eight cc. of water. This produced an effervescence of hydrocyanic acid. It was transferred to tubes and allowed to stand for several hours, during which time the solution became dark reddish brown in color. These tubes were heated the same as No. 6 and appeared about the same. They were combined and evaporated as before, and enough of sulphuric acid added to satisfy one-half the potassium cyanide. The contents of the two tubes were extracted with ether as previously described, the crystals looked about the same as those obtained by No. 6 and melted at 162°C . The yield was 0.175 gram; theory, 2.9 grams.

ATTEMPTS TO MAKE β CYANPROPIONIC ACID FROM ETHYL
ETHER OF β IODOPROPIONIC ACID.

No. 8. As the ethyl ether of chloracetic acid on treatment with potassium cyanide gives cyanacetic acid, it seemed probable that the ethyl ether of β iodopropionic acid would give β cyanpropionic acid. It was with this hope that the following experiments were undertaken.

The iodo acid had first to be converted into the ether which was done as follows: 200 grams of β iodopropionic acid, 100 grams of ethyl alcohol, and twenty grams of sulphuric acid were mixed in a round-bottomed flask and heated on a water-bath with a return condenser for five and a half hours. The liquid had then separated into two layers. It was transferred to a separator and washed, first with sodium carbonate solution and then with water. The ether, a dark, heavy liquid, was then separated and dried. The yield was 125 grams.

To convert the ether into the cyan acid I used an excess of potassium cyanide over the two molecules required by the reaction.



To 145 grams of the ether were added ninety-three grams of potassium cyanide dissolved in 372 grams of water. This mixture was made in a round-bottomed flask in which it was left to stand for twenty hours, the ether forming a separate layer. It was then heated with a return condenser for ten hours; at the end of five hours the layers had mixed and the whole solution was a dark brown in color. On removing from the flask, a dark oil was seen floating on the liquid and to obtain this it was shaken with ether twice, the ether extracts separated, and the ether distilled off; the residue was a brown oil which was tested for nitrogen by the prussian blue reaction but none was found. It, however, gave a decisive test for iodine, and was the unaltered ether of β iodopropionic acid.

The solution from which the unaltered ether had been removed was made almost neutral with sulphuric acid and evaporated on a water-bath to dryness. It was then made acid with dilute (normal) sulphuric acid and shaken twice with liberal quantities of ether. The residue, a brown liquid, was made strongly acid

with sulphuric acid and shaken with ether three times. The residue from this treatment was evaporated to dryness on a water-bath and extracted with ether three times more.

The three different ether solutions, supposed to contain the cyan acid, were distilled separately and the residues kept to convert into the lead salt of cyanpropionic acid as a means of purifying the product. To do this they were shaken with lead carbonate in excess and then the lead sulphate and carbonate filtered out. The formation of the lead salt gave a lively effervescence with the first two lots but failed to give any with the third, so I considered that none of the cyan acid was removed by the last extractions.

The filtrates described above were saturated separately with hydrogen sulphide, which gave a copious precipitate of lead sulphide. The solutions were filtered and the filtrates combined and evaporated on a water-bath to dryness. It was then found that the lead had not been entirely removed, so the mass was redissolved in hot water, and hydrogen sulphide passed in again. It was filtered and washed as before and evaporated on a water-bath. On cooling, the substance turned solid.

The solubility of this substance is as follows :

| | Cold. | Warm. |
|------------------------|----------------|------------------|
| Ether..... | insoluble | almost insoluble |
| Ethyl alcohol..... | slowly soluble | soluble |
| Chloroform | insoluble | insoluble |
| Carbon disulphide..... | insoluble | insoluble |
| Methyl alcohol | insoluble | soluble |
| Acetone | insoluble | insoluble |
| Benzene | insoluble | insoluble |

Some of this product was recrystallized from both ethyl and methyl alcohol and the melting points determined. The results were as follows :

| | |
|---------------------|-----------|
| Ethyl alcohol..... | 110°-111° |
| Methyl alcohol..... | 109°-110° |
| Crude..... | 154° |

A small sample was recrystallized from methyl alcohol several times and its melting point determined. It began to melt at 117° but part remained solid until 144° was reached, when all melted, indicating in spite of repeated recrystallizations that the sample was a mixture.

No. 9. This method is a slight modification of the preceding.

Ninety grams of potassium cyanide were dissolved in 300 cc. of water and added to 142 grams of the ethyl ether of β iodopropionic acid in a round-bottomed flask as before. This was heated on a water-bath with a return condenser for twelve hours to try to ensure the entire conversion of the ether; it was then shaken with ether in a separator to recover the unaltered ether, and in spite of the increased time during which the mixture was heated thirty-five grams of the ether were obtained.

The under layer from the separator was neutralized with sulphuric acid and evaporated on a water-bath to a syrup. It was made acid with dilute sulphuric acid (one to one) and shaken with ether in a separator three times, using liberal amounts of ether each time.

(The object of first neutralizing and afterwards making acid was to avoid as far as possible, heating with acid which might form succinic acid.) The ether solutions were of a dark reddish color, much darker than those obtained in No. 8. The ether was distilled off, the residue diluted with water, shaken with lead carbonate, filtered, washed, the filtrate saturated with hydrogen sulphide as before, the lead sulphide filtered out and the solution evaporated on the water-bath.

The residue from the ether extraction was evaporated on a water-bath until on cooling it turned solid, and was then transferred to a separator and made much more strongly acid with dilute sulphuric acid, and was well mixed and shaken three times with ether. The ether solution was treated as before, and after removing the lead, was added to the first portion and evaporated to dryness with it. The solid mass was then crystallized twice from methyl alcohol.

To the residue from the second ether extraction in the separator, water was added and the solution filtered, the residue was rejected, and to the filtrate, litharge and lead carbonate added until all the acid present which was mostly sulphuric was neutralized. It was next filtered and hydrogen sulphide passed in. A precipitate of a dark red brown color was obtained instead of the black lead sulphide. This precipitate was filtered out and was found to contain lead and sulphur, was soluble in hot

dilute nitric acid and in concentrated hydrochloric acid, but insoluble in dilute sulphuric. This red precipitate sometimes forms at other times when the solution supposed to contain the lead salt of β cyanpropionic acid is saturated with hydrogen sulphide, but it was always either subsequently decomposed or obscured by the quantities of black sulphide which formed later.

This compound is apparently similar to the lead chlorosulphide described by Fresenius (page 173 Qual. Anal.), but in which some organic acid replaces the hydrochloric acid.

The filtrate from this precipitate was evaporated to dryness on the water-bath and extracted with ether four times. The ether was distilled off and the resulting crystals recrystallized from methyl alcohol.

Total yield, 2.6 grams, having a melting point of 124° C.

INVESTIGATION OF CRYSTALS MADE BY THE
PRECEDING METHODS.

Combustions were made on the crystals obtained by methods 8 and 9. The amount of moisture was also determined by drying so as to calculate the percentage to the dry if possible. The results were as follows:

No. 8 gave—

| | |
|--|-----------------|
| Carbon..... | 38.95 per cent. |
| Hydrogen..... | 6.39 " " |
| Nitrogen..... | 11.62 " " |
| Loss on drying for five hours at
from 90° to 107° | 12.31 " " |
| Nitrogen, on dried sample..... | 8.07 " " |

These results calculated to the dry measure gave—

| | |
|---------------|-----------------|
| Carbon..... | 44.42 per cent. |
| Hydrogen..... | 5.72 " " |
| Nitrogen..... | 13.25 " " |

These combustions were made very carefully and I believe them to be correct. The figures agree quite closely with the percentage composition of $C_6H_7N_2O_5$, which is

| | |
|---------------|-----------------|
| Carbon | 44.44 per cent. |
| Hydrogen..... | 5.55 " " |
| Nitrogen..... | 12.97 " " |

This might be formed by two molecules of β cyanpropionic acid taking up one molecule of water and combining, $2C_3H_5NO_2 +$

$\text{H}_2\text{O} = \text{C}_6\text{H}_{11}\text{N}_3\text{O}_8$, or it may be written $\text{C}_6\text{H}_7\text{NO}_5 + \frac{1}{2}\text{H}_2\text{O}$. The melting point of crystals from No. 8, on which these combustions were made, was 110°C .

No. 9 gave—

| | |
|---------------|-----------------|
| Carbon | 37.15 per cent. |
| " | 37.27 " " |
| Nitrogen..... | 6.34 " " |
| " | 6.19 " " |
| Hydrogen..... | 5.77 " " |
| " | 5.79 " " |

Loss on drying to constant weight for eighteen hours at 100° – 110° , 13.22 per cent.

These determinations of the carbon, hydrogen, and nitrogen, calculated to the dry gave—

| | |
|---------------|-----------------|
| Carbon | 42.88 per cent. |
| Hydrogen..... | 4.96 " " |
| Nitrogen..... | 7.22 " " |

A nitrogen combustion was made on the crystals from Nos. 6 and 7, which gave further evidence of the loss of nitrogen by heating as the crystals obtained by these methods contained but 3.02 per cent. nitrogen.

The crystals from methods 8 and 9 were dissolved in water and tested with methyl orange to see whether they would give an acid reaction, but they did not. They only gave the color of a neutral solution. Succinimid (M. P. 124) was tried which gave the same color. Cyanacetic acid was also tried but this gave a bright pink. From this it was evident that the crystals could not be β cyanpropionic acid or they would turn the indicator like cyan acid.

The mother liquor from method No. 5, in which the crystals were slowly forming, was tested in the same way and it gave a decided pink color. To make sure this was not due to any mineral acid, I tested for sulphuric acid with barium nitrate but found none. (Sulphuric was the only acid used in the method.)

I now believe that β cyanpropionic acid is a liquid and is formed in many of the preceding methods, but that it decomposes very readily by heat or pressure, forming various complicated organic compounds, which are the crystals obtained. Another reason for my thinking so is that methods 6 and 7 which

are heated in sealed tubes, on evaporating gave crystals direct, while in the methods which were not heated so much a syrupy liquid was left, which only deposited crystals after standing in some cases for weeks over sulphuric acid, showing the complete decomposition of the acid in the first case and but the partial in the second as it was there the acid reaction was obtained. The irregularity of the combustion is explained by the fact that the samples must have been in most cases, mixtures. The only combustions which agree very well are those made on the same day on a sample of No. 9 which had been recrystallized four times.

The diminished percentage of nitrogen in the methods where longer or higher heat was used, and also where the sample was afterwards dried, seems to be invariable and points to a decomposition in which nitrogen is lost.

The nearest approach to β cyanpropionic acid so far produced is its ethyl ether which has been made by L. Henry,¹ as follows:

Heat $\text{CH}_3\text{ICH}_2\text{COOC}_2\text{H}_5$ with potassium cyanide dissolved in alcohol in slight excess on a water-bath with a return condenser. The reaction takes place easily and potassium iodide is deposited abundantly; at the end the liquid turns brown. Drive out as much of the alcohol as possible by distilling on the water-bath and extract the cyan ether with ordinary ether. The distillation of the ether solution gives the pure cyanpropionic ether. The yield is almost theoretical.

The cyanpropionic ether is a colorless liquid, without odor, insoluble in and more dense than water, and boils at 228° . Caustic potash in aqueous alcohol transforms it easily into normal potassium succinate. With aqueous ammonia it gives cyanpropionic amide $\text{CN}(\text{CH}_2)_2\text{CONH}_2$.

The preceding facts were not known to me at the time I made my experiments on iodopropionic ethyl ether or I should have tried alcoholic cyanide, and so by the elimination of water, would have probably succeeded in obtaining the ethyl ether and amide of β cyanpropionic acid, if not the acid.

My experiments show that the β iodopropionic ethyl ether does not act with potassium cyanide like the ethyl ether of chloroacetic, as by treating the latter with potassium cyanide as

¹ L. Henry, *Bull. d. l'acad. royal de Belgique*, [3] 18, 168, 1889.

described under the first method in which the ether was used, I obtained a good yield of cyanacetic acid without difficulty.

The reactions between nitriles and both fatty and aromatic acids will be more fully developed in this laboratory.

ORGANIC LABORATORY, SCHOOL OF MINES,
COLUMBIA COLLEGE, MARCH, 1894.

THE DETERMINATION OF PHOSPHORIC ACID.

BY S. W. JOHNSON.

Received April 25, 1894.

THE papers on determination of phosphorus in steel by Messrs. Dudley and Pease, by Mr. Handy, and by Messrs. Doolittle and Eavenson, remind me of some work done at my instigation in the years 1880, 1889, and 1890, and published in the Annual Reports of the Connecticut Agricultural Experiment Station for those years.

In 1880, Mr. (now Professor) H. L. Wells, demonstrated that the citrate method for determining phosphoric acid may give good results under certain conditions, but that the results are correct because of a compensation of errors, the ammonium magnesium phosphate not carrying down quite all the phosphorus but containing enough impurities to counterbalance that loss. Over ninety determinations were made, many of them in duplicate, on forty different substances (fertilizers), after a large number of preliminary trials had indicated the effect of varying the several conditions which might influence the results. In most cases the percentages of phosphoric acid found in duplicate agreed well together and also agreed fairly with those given by the molybdate method. In a few cases, however, considerable discrepancies appeared and it was evident that further study was needful before the citrate method could be fully trusted for fertilizer work.

In 1889, in conjunction with Dr. T. B. Osborne, investigation of the citrate method was resumed. The German agricultural chemists were beginning to use it and J. H. Vogel had published details of procedure. We found that Vogel's process gave results too low and not closely agreeing with the molybdate method. By using more and stronger magnesium mixture and a larger quantity of concentrated ammonia, we overcame this discrepancy, and in sixty-seven determinations on bone-dust superphosphates, cotton-hull ashes, cotton-seed meal, tankage,

bone char, phosphatic guano, and phosphate rock, we found that but three citrate determinations differed from those by molybdate, by more than 0.3 per cent., and but four others by more than 0.2 per cent. The greatest discrepancy between the two methods was 0.41 per cent., while the average difference was 0.09 per cent. In thirty cases the citrate method averaged 0.117 per cent. more, in thirty-three cases 0.079 per cent. less, than the molybdate method. These percentages were reckoned on 0.4 gram of substance containing from 0.5 to 31.5 per cent. of P_2O_5 . The determinations were not made with unusual care, but were turned off rapidly as a part of the routine work of the station.

The citrate method was found to give unsatisfactory results where iron and alumina were present in considerable quantity, as in case of "Grand Cayman's Rock," "Thomas Gilchrist Slag," and "Keystone Phosphate." A series of trials under varied conditions was made in 1889 with the hope to ascertain the cause of the discrepancies but without success.

Some analyses of the ignited precipitate obtained by the citrate method may be quoted here:

COMPOSITION OF IGNITED "CITRATE PRECIPITATES."

| | Bone. | Super-phosphate. | Grand Cayman's phosphate. | South Carolina rock. | Bolivian guano. | Dis-solved bone black. |
|------------------------------------|--------|------------------|---------------------------|----------------------|-----------------|------------------------|
| Carbon..... | 0.41 | 0.19 | 0.44 | 0.15 | 0.48 | 0.27 |
| Silica | | 0.12 | 0.40 | 0.10 | 0.24 | 0.19 |
| Calcium oxide..... | 2.59 | 2.13 | 2.05 | 3.21 | 3.95 | 2.05 |
| Magnesium pyrophosphate | 95.49 | 96.07 | 95.66 | 95.77 | 94.98 | 97.83 |
| Ferric and aluminum phosphate..... | | | 0.71 | 0.35 | | 0.31 |
| Loss | 1.51 | 1.49 | 0.74 | 0.42 | 0.35 | |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.65 |

The loss probably consisted in part, of magnesia and in part also of pyrophosphoric acid. It is seen that the ignited precipitates contained from two to four per cent. of lime, that iron and alumina entered into the precipitate in small quantity when these elements were abundant in the original substance, and that where there was little or no loss, the recovered phosphoric acid amounted to from 95 to 97.8 per cent. of the precipitate.

In case of Grand Cayman's phosphate rock, duplicate determinations differed as much as 0.3 per cent., and the variations of duplicates of Thomas Slag and Keystone phosphate were even greater. It was also found that by changing the proportions of the reagents and by using on the one hand moderate and on the other vigorous and prolonged agitation, the quantity of phosphoric acid, reckoned from the ignited precipitate, fluctuated, in case of Thomas slag and Keystone phosphate, $2\frac{1}{2}$ and $3\frac{1}{2}$ per cent., respectively, although by using large quantities of magnesia mixture and of strong ammonia, accordant and high results were realized.

Thus far we employed the modified rapid molybdate method, precipitating from hot solutions and digesting for one hour at 65° C. Finally in 1890 we found that under this procedure, the molybdate method, though satisfactory in absence of ferric, aluminum, and manganese salts, is, in their presence, little better than the citrate method. In case of Keystone phosphate three determinations by Osborne, using the U. S. "official" method gave figures ranging from 45.25 to 46.68 per cent.!

It was therefore necessary to return to the original Sonnenschein method and make the precipitations at 40° to 50° C., during six hours. Six determinations thus carried out by Osborne, gave results from 44.67 to 44.86, the average being 44.82 per cent.

Comparative duplicate trials on a carefully made up solution of known composition with $P_2O_5 = 18.93$ per cent.¹ (from crystallized sodium phosphate) $Fe_2O_3 = 20$ per cent., $Al_2O_3 = 4.72$ per cent., and $MnO = 5.09$ per cent. (from sulphates), yielded Osborne, by the original Sonnenschein method, 18.92 and 18.94 per cent., and by the "official" method 19.26 and 19.26 per cent.!

We proved that with relative excess of nitric acid or relative deficiency of molybdic acid, a portion of phosphoric acid may easily fail to be thrown down. We also found that when precipitation is made hot and digestion is conducted at 65° C., ferric iron, and aluminum, if present, are to some extent included in the yellow precipitate and when this is dissolved in the subsequent treatment with ammonia, they pass into the alkaline

¹ Determined in the usual manner as magnesium pyrophosphate.

solution and thence into the ammonium-magnesium phosphate.

To sum up, the citrate method only gives good results by compensation of its errors and under exactly defined conditions which must be empirically determined. A procedure good for calcium phosphates is quite inapplicable to ferric and aluminum phosphates.

Again, the molybdic method, when carried out rapidly at temperatures higher than 50°, or as high as 65° C. in presence of trivalent iron, aluminum, or manganese, gives results too high, and in presence of great excess of nitric acid may give results too low, unless the filtrates from the yellow precipitate are mixed with additional molybdic solution and further digested until no more precipitate can be thrown down.

DOUBLE BROMIDES OF PALLADIUM.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

Received May 5, 1894.

BONSDORFF (*Poggendorff's Annalen der Physik*, [1], N. F., 19, 347) was one of the first chemists to attempt the preparation of double halides of palladium with other metals. Beyond mere mention of the fact that he obtained palladium bromide by the action of a mixture of nitric and hydrobromic acids upon the metal, that the resulting compound apparently combined "mit den Bromiden elektro-positiver Metalle," and that he made double salts of it with the chlorides of potassium, barium, manganese, and zinc, we have not discovered any additional literature relating to the above subject. It does not appear that Bonsdorff analyzed any of the double halides obtained by him.

Desirous of finding a salt or salts of palladium suitable for, but as yet not used in atomic mass determinations of palladium, we took occasion to prepare several double bromides of that metal, hoping to find among them one or more which might be available for the purpose.

Very pure metallic palladium was dissolved in nitro-hydrobromic acid. The residue was moistened with hydrobromic acid and repeatedly evaporated to dryness upon a water-bath. The palladium bromide, reddish-brown in color, was only soluble in water containing hydrobromic acid. Weighed quantities of this

dry bromide, with equivalent amounts of the metallic bromides, were dissolved in water containing hydrobromic acid. Upon evaporation, crystalline residues were obtained. These were always dissolved in water and again allowed to separate.

POTASSIUM PALLADIUM BROMIDE.



This salt separated from its aqueous solution in shining reddish-brown needles. It is anhydrous. It is very stable and suffers no change on exposure to the air. In analyzing it we determined the palladium by the method suggested by Frenkel, *Ztschr. anorg. Chem.*, 1, 229. By following this recommendation the bromine can be precipitated by silver nitrate without contamination with palladium.

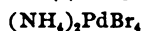
Analysis.—0.4930 gram dried material gave 0.1045 gram metallic palladium, equal to 21.19 per cent. Pd, and 0.7428 gram silver bromide, equal to 63.79 per cent. Br, while the theoretical requirements of K_2PdBr_4 are 21.12 per cent. Pd and 63.50 per cent. Br. A second portion of substance, weighing 0.2613 gram, was gently heated in a current of hydrogen and, after cooling, the residue was extracted with hot water. Upon evaporating this aqueous solution to dryness, 0.1251 gram of potassium bromide was obtained. This is equal in percentage to 15.58 per cent., while the theoretical potassium bromide in this double salt is 15.45 per cent.

Hoping that by adding bromine to the aqueous solution of the above salt, and digesting the same with this reagent, at a temperature not exceeding 70° , we might possibly get a salt of the formula K_2PdBr_4 , we carried out several such experiments. The result was not what was anticipated; the product being really a salt of the simpler type, K_2PdBr_4 , with two molecules of water of crystallization, $\text{K}_2\text{PdBr}_4 \cdot 2\text{H}_2\text{O}$. It separated in long, dark-brown and shining needles, which on exposure rapidly lose their luster, become dull, and acquire a reddish-brown color. Owing to the rapid loss of water by the crystals, the analytical results do not approach the theoretical requirements as closely as might be expected.

Analysis.—0.3235 gram substance gave 0.0660 gram, or 20.37 per cent. of metallic palladium; 0.4565 gram of silver bromide,

equal to 60.00 per cent. of bromine and 0.0201 gram of water, equivalent to 6.21 per cent. The formula $K_2PdBr_4 + 2H_2O$ requires 19.71 per cent. Pd, 59.2 per cent. Br, and 6.65 per cent. H_2O .

AMMONIUM PALLADIUM BROMIDE.



This salt crystallizes in beautiful and quite large olive-brown colored forms which apparently possess an orthorhombic habitus. They are anhydrous and are perfectly stable in ordinary air. They possess about the same solubility as the corresponding potassium salt.

Analysis.—0.2528 gram dry material gave 0.0585 gram metallic palladium, equal to 23.14 per cent., and 0.4090 gram silver bromide, equivalent to 68.82 per cent. of bromine, while the theoretical percentages are $Pd = 22.91$, and $Br = 69.17$.

As this salt and the corresponding potassium salt are anhydrous and can be obtained pure without great difficulty, it is our intention to use them in a redetermination of the atomic mass of palladium.

SODIUM PALLADIUM BROMIDE.

We experienced much trouble in getting this salt, and it was only after the solution, containing equivalent amounts of sodium and palladium bromides, was allowed to remain in a vacuum desiccator over concentrated sulphuric acid for some time that it separated out in large deep red colored plates which proved to be very deliquescent. It was therefore necessary to conduct the analysis with imperfectly dried material. Through an accident we are not able to give a result upon the bromine content, and are limited to a presentation of the palladium and water percentages. These are, 19.68 per cent. Pd, and 14.67 per cent. H_2O . A salt of the composition $Na_2PdBr_4 + 4\frac{1}{2}H_2O$ would require 19.25 per cent. Pd, and 14.63 per cent. H_2O .

This salt is very deliquescent and even to a much greater degree than the corresponding double chloride of sodium and palladium.

STRONTIUM PALLADIUM BROMIDE.

The solution of this salt also stood for many days before crystals made their appearance. It consists of short, black prisms, which are stable on exposure to the air.

Analysis.—0.2256 gram air-dried substance gave 0.0366 gram Pd, or 16.22 per cent.; 0.2643 gram silver bromide, or 49.82 per cent. Br, and 0.0679 gram strontium sulphate, equal to 14.09 per cent. strontium.

A second analysis gave 0.0518 gram Pd, or 16.79 per cent.; 0.3595 gram silver bromide, or 49.57 per cent. Br; 0.0861 gram strontium sulphate, equal to 13.29 per cent. Sr, and 0.0544 gram water, corresponding to 17.63 per cent.

A salt of the composition $\text{SrBr}_2 \cdot \text{PdBr}_2 + 6\text{H}_2\text{O}$ would require

| | | |
|-------|-----------|------------------|
| 17.11 | per cent. | Pd |
| 13.99 | " " | Sr |
| 51.47 | " " | Br |
| 17.37 | " " | H ₂ O |

Our deficiency in bromine, we believe, is due to a slight loss of that constituent occurring during the drying process.

MANGANESE PALLADIUM BROMIDE.

This salt is very soluble in water. Like the two preceding salts it only separated from its aqueous solution after long standing. Its crystalline form is apparently like that of the ammonium salt. The crystals are dull-black in color.

Analysis.—0.1829 gram air-dried substance was carefully heated to constant weight in an air-bath. The loss, representing water, equaled 20.39 per cent. The anhydrous residue was then exposed at a moderate temperature to the action of hydrogen gas. On cooling, the mass was extracted with dilute hydrochloric acid. The spongy palladium weighed 0.0331 gram, equal to 18.09 per cent. Pd. The filtrate from the palladium gave 9.29 per cent. of manganese.

These results indicate a salt with the formula $\text{MnPdBr}_2 + 7\text{H}_2\text{O}$, which would require

| | | |
|-------|-----------|------------------|
| 17.52 | per cent. | Pd |
| 9.05 | " " | Mn |
| 20.73 | " " | H ₂ O |

An effort was made to prepare the double halides of zinc and of cadmium with palladium, but the products crystallized so poorly that the analysis of the same was abandoned.

UNIVERSITY OF PENNSYLVANIA,
April 25, 1894.

AN EXAMINATION OF THE CHLORIDES OF ZIRCONIUM.

BY F. P. VENABLE.

Received April 16, 1894.

A ZIRCONIUM chloride of definite composition would prove a valuable compound for determining the atomic weight of the element. There are several difficulties in the way of securing such a compound.

1. The tendency to form basic chlorides.
2. The ease with which hydrochloric acid is lost through the action of heat and of dehydrating agents.
3. The presence of free hydrochloric acid.
4. The deliquescent nature of the chlorides.

It is particularly desirable that the conditions under which a definite chloride can be formed should be discovered, as zirconium seems to yield no very satisfactory compounds for the determination of the atomic weight. There have been many efforts at finding out these exact conditions.

Most text-books state that anhydrous, pure zirconium tetrachloride can be prepared by passing dry chlorine over a mixture of charcoal and zirconia heated to a high temperature. Hermann used this sublimed zirconium chloride for the determination of the atomic weight. As Clarke says, however, little confidence can be placed in his results. Bailey¹ has recorded that even with great care to avoid the presence of moisture he was unable to prevent the formation of oxychlorides. He also says that in no case was it found possible to prepare the chloride free from iron and silica. The necessity for the presence of these in the materials used or in the resulting compounds is not very apparent. I have as yet had no opportunity of repeating his experiments.

The chlorides most commonly worked with, have been those formed by the solution of the hydroxide in hydrochloric acid, followed by precipitation or crystallization from concentrated hydrochloric acid.

Berzelius attempted to remove the excess of hydrochloric acid

¹ *Chem. News.*, 60, 17.

by heating the salt to 60° C. but was not able to obtain a definite compound. Two analyses gave

| | | |
|------------------------|-------|-------|
| ZrO ₂ | 0.332 | 0.485 |
| AgCl | 0.661 | 1.096 |

The silver chloride should be about two and one-third times as much as the oxide.

Paykull dried the salt between filter paper and found the composition of the crystals to be $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, the amorphous form precipitated by hydrochloric acid being $2\text{ZrOCl}_2 \cdot 13\text{H}_2\text{O}$.

Endemann has described basic or oxychlorides $\text{Zr}_2\text{O}_3\text{Cl}_2$, ZrOClOH , and $\text{Zr}_2\text{O}_3\text{Cl}_2(\text{OH})_2$; Troost and Hautefeuille have described others, $\text{Zr}_2\text{O}_3\text{Cl}_2$ and Zr_2OCl_2 . In fact water is so easily taken up and hydrochloric acid lost that a large number of such indefinite compounds might be prepared by slightly varying the conditions.

Nylander¹ made a series of attempts at dehydrating the chloride. He prepared the chloride by dissolving the hydroxide in hydrochloric acid and evaporating to crystallization. The salt formed white needles, easily soluble in water. They were washed with alcohol and for analyses I and II were pressed between filter paper; III and IV were dried over sulphuric acid. The results were as follows:

| | I. | II. | III. | IV. |
|----------------------------|-------|-------|-------|-------|
| Zr..... | 27.56 | 25.69 | 30.11 | 31.78 |
| Cl..... | 21.58 | 21.58 | 23.06 | 23.80 |
| Loss (H ₂ O)... | 50.86 | 52.78 | 46.83 | 44.12 |

or calculated on a dry basis:

| | | | | |
|---------|-------|-------|-------|-------|
| Zr..... | 56.08 | 54.41 | 56.63 | 57.18 |
| Cl..... | 43.02 | 45.59 | 43.37 | 42.82 |

Again preparations were made as before. I was dried between filter paper, II over sulphuric acid, III was pressed between filter paper and then dried over sulphuric acid, IV was dried a long time over sulphuric acid. The analyses gave the following:

| | I. | II. | III. | IV. |
|------------|-------|-------|-------|-------|
| Zr..... | 28.52 | 34.91 | 37.78 | 35.69 |
| Cl..... | 21.93 | 26.09 | 25.87 | 21.74 |
| Loss | 49.55 | 39.10 | 36.35 | 42.57 |

or calculated on a dry basis:

| | | | | |
|---------|-------|-------|-------|-------|
| Zr..... | 56.93 | 57.23 | 59.34 | 62.14 |
| Cl..... | 43.07 | 42.77 | 40.66 | 37.86 |

Lastly he allowed a solution of the chloride to evaporate over

¹ Bidrag till kännedomen om Zirkonjord. Inaug. Diss. Lund, 1864.

sulphuric acid washed the crystals obtained with alcohol and pressed them between filter paper. Analyses gave:

| | | |
|------------|-------|-------|
| Zr | 27.94 | 28.74 |
| Cl | 27.32 | 26.67 |
| Loss | 44.74 | 42.62 |

or calculated on a dry basis:

| | Found | | | Theory. |
|---------|-------|-------|-----------------------|---------|
| Zr..... | 50.56 | 50.04 | Zr..... | 38.50 |
| Cl..... | 49.44 | 49.96 | Cl ₄ | 61.50 |

The above results show that his preparations were indefinite oxychlorides or mixtures in varying proportions of zirconium tetrachloride and oxychloride.

Bailey repeatedly crystallized the chloride from hydrochloric acid, washed it with hydrochloric acid and then removed the free acid.

(1) By washing with a mixture of one part alcohol and ten parts of ether.

(2) By gently heating the salt.

(3) By exposing the finely divided salt at ordinary temperatures in a vacuum desiccator over potash until no hydrochloric acid appeared when air was passed over it.

The analysis was performed by dissolving the salt in water and precipitating the zirconia with ammonia, then acidulating with nitric acid and precipitating the chlorine by means of silver nitrate. By method (2) a constant and progressive diminution of chlorine was observed. Therefore no analyses were made. For the other methods he gives the results of the analyses by a statement of the relation of ZrO_2 to $AgCl$.

| | ZrO_2 : | $AgCl$ |
|-------------------------------|-----------|---------|
| Berzelius determination | I | : 1.991 |
| " " | I | : 2.260 |
| Bailey's method I..... | I | : 2.206 |
| " " "..... | I | : 2.179 |
| " " "..... | I | : 2.226 |
| " " "..... | I | : 2.260 |
| " " 2..... | I | : 2.264 |
| " " " without washing | I | : 2.245 |
| " " "..... | I | : 2.309 |
| " " "..... | I | : 2.285 |
| $ZrOCl_2$ | I | : 2.350 |

These preparations are evidently mixtures also.

Hermann¹ states that the hydrated chloride, gotten in crystals on evaporating its aqueous solution, becomes opaque at 50° C., giving off part of the water and half of the hydrochloric acid and leaving a basic chloride or oxychloride, $\text{ZrCl}_4 \cdot \text{ZrO}_2 \cdot 18\text{H}_2\text{O}$ or $\text{ZrOCl}_2 \cdot 9\text{H}_2\text{O}$. The same compound is obtained in stellate groups of white silky prisms on evaporating a solution of the chloride. These crystals when heated become white and turbid and are converted into the anhydrous dioxychloride, $\text{ZrCl}_4 \cdot 2\text{ZrO}_2$.

The conditions here are inexact and though Hermann may have obtained these compounds he would doubtless find it difficult to prepare them again. While it is perfectly true that an oxychloride is formed on the evaporation of an aqueous solution of the chloride, I have been unable to obtain the compounds he mentions. Linnemann² maintains that crystallization from hydrochloric acid (sp. gr. 1.17) and treatment with alcohol and ether gives a fine, crystalline, snow white, silky body, leaving fifty per cent. of its weight on ignition and therefore very nearly pure ZrCl_4 which should leave 52.5 per cent. He claims that this is "chiefly a neutral, not a basic compound."

My own experiments on the dehydration of this salt have extended over the past two years, as opportunity was afforded. Several series of experiments were undertaken, some along the lines attempted by others, and others by methods not tried before. In all the purified chloride obtained by repeated crystallization from hydrochloric acid was used, the salt being still wet with the excess of the acid. There was no attempt at drying this between filter paper. The method of preparing this salt has been fully described in a previous paper in the *Journal of Analytical and Applied Chemistry*, 5, 551.

In the first experiment this chloride was washed once with water and then put in a desiccator and dried over calcium chloride (porous desiccated). It remained in the desiccator about seven months. Even after this lapse of time it still continued to show a slight loss in weight. It yielded on analysis 48.84 per cent. ZrO_2 .

Another portion was placed in a jar over solid lumps of sodium hydroxide. After six weeks the loss was very slight. Careful

¹ Watts' Dict., 5, 1080.

² Chem. News., 52, 224.

ignition left a residue of ZrO_2 , equivalent to 42.99 per cent. of the original weight. There was found to be 24.44 per cent. of chlorine present.

Again a portion was placed over calcium chloride and dry air was drawn over it at the rate of about fifty liters in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued, although it was slight. On analysis this gave ZrO_2 , 42.28 per cent., and Cl 24.35 per cent. Although the results in this and the experiment immediately preceding correspond fairly well, they are unsatisfactory as they point either to a mixture of chlorides or an oxychloride of very complicated formula and hence unsuited for the ultimate aim of the research.

Lastly a portion was placed over concentrated sulphuric acid and the atmosphere above it exhausted occasionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about 0.02 per cent. of the whole. The mass was powdery with a slightly discolored crust. It was all soluble in water, however, and yielded a clear colorless solution. It contained 53.30 per cent. of ZrO_2 . This corresponds very nearly to the formula ZrCl_2 , and is altogether at variance with the results obtained by Nylander and with the assertion made by Hermann that half of the hydrochloric acid was lost over sulphuric acid.

This last experiment showed the possibility of securing pure zirconium chloride, provided the excess of hydrochloric acid could be removed. It was thought that this might be done by heating in an atmosphere of hydrochloric acid. A weighed flask was so arranged that it could be kept at a definite temperature while a stream of dry hydrogen chloride was passing through it. The temperature ranged from 100° to 110°C. , and the chloride placed in the flask melted, solidifying again after the loss of the water and excess of hydrochloric acid. If the drying was done slowly enough, fine crystals of zirconium chloride were gotten which lost no further weight on being kept at 100°C. A

more rapid drying left a hard white mass which was quite hygroscopic. Heating this mass for several days did not cause any diminution in weight, provided the flask was kept full of hydrogen chloride. If the mass was heated even a short time in the absence of hydrogen chloride then further heating caused a continuous loss of weight even in the presence of a rapid stream of hydrogen chloride. After this it was impossible to secure a constant weight.

This method of drying has been tried repeatedly on various preparations and I regard the facts stated above as showing conclusively that a neutral zirconium chloride can be prepared and dried.

Analyses of this chloride gave the following percentages of ZrO_2 :

| | | |
|-------|-------|-------|
| 52.70 | 52.78 | 52.63 |
|-------|-------|-------|

Experiments have already been begun with a view of utilizing this body in a series of experiments looking to a revision of the atomic weight of zirconium.

In connection with this subject it may be well to mention some improvements in the method of purifying zirconium chloride. (See *Journal of Analytical and Applied Chemistry*, 5, 551.)

In the first place the separation from silica by evaporation to dryness is not complete. It is impossible to heat this chloride to the necessary temperature without such a decomposition as will render the zirconium chloride also insoluble. It is best then to make this separation as thorough as possible by heating, then to change the chloride into oxide by ignition and to treat this several times with hydrofluoric acid until the trace of silica is all driven off. This silica is too small in amount to interfere with ordinary uses but would have to be removed where perfect purity was demanded.

Again where the hydroxide is dissolved in dilute hydrochloric acid, or contained so much water that the acid was greatly diluted by it, it will be found that more or less of a white insoluble powder will form on evaporating, as recommended on a water-bath, and on subsequent treatment with boiling strong hydrochloric acid. By a careful arrangement of glass wool in a hot-water funnel the dissolved chloride can be filtered away from

this insoluble mass. It seems to be quite insoluble in hydrochloric acid though easily dissolved by water. Analysis shows that this mass is ZrOCl_2 and with it was found, as an impurity, whatever silica the separation by heating failed to remove.

Lastly, my assistant, Mr. Baskerville, has shown that much time and hydrochloric acid will be saved if, in the solutions containing much iron, the zirconium hydroxide be first precipitated out by means of sulphur dioxide. This precipitate can then be dissolved in acid and purified by crystallization as already recommended.

Of course it need scarcely be mentioned that if silica has been removed by ignition and treatment with hydrofluoric acid, it will be necessary to fuse once more with caustic alkali and repeat the ordinary purification.

UNIVERSITY OF NORTH CAROLINA,

April 12, 1894.

SEPARATION OF ZIRCONIUM BY MEANS OF SULPHUROUS ACID.

BY CHARLES BASKERVILLE.

Received April 16, 1894.

WHILE testing the accuracy of the various methods recommended for the estimation of zirconium I was led, because of the analogy of the elements, to try a method commonly used with titanium; *viz.*, prolonged boiling of a potassium bisulphate fusion in dilute solution with sulphurous acid in excess. On application of this method, however, on a solution of zirconium sulphate (prepared by dissolving the hydroxide in sulphuric acid), I failed even after boiling four hours with an excess of sulphur dioxide to obtain a precipitate, if the solution was acid. If the solution was nearly neutralized with ammonium hydroxide and then boiled with an excess of sulphur dioxide, after being greatly diluted, a precipitate was produced. This precipitation, however, was incomplete, even after boiling six hours or passing steam through the same for two or three hours. The precipitate too was very finely divided, running through all filter papers at my command. Therefore this method could not be used.

But an addition of sulphurous acid to a solution of zirconium chloride, even in a cold acid solution, a dense white precipitate was immediately noted. On boiling with an excess of sulphurous

acid in a neutralized solution, *i. e.*, the hydrochloric acid solution neutralized by ammonium hydroxide until the slight precipitate formed was no longer dissolved on boiling, and this precipitate then taken up with two or three drops of dilute hydrochloric acid, the zirconium was completely precipitated.

The accuracy of the method is seen in the following results:

| | Found. | Used. |
|------------------------|--------|--------|
| ZrO ₂ | 0.1074 | 0.1077 |
| " | 0.1078 | 0.1077 |
| " | 0.1043 | 0.1038 |
| " | 0.1070 | 0.1077 |
| " | 0.1047 | 0.1050 |

The precipitation took place immediately on addition of sulphurous acid, and after two minutes boiling the precipitate settled quickly and was easily filtered.

This method then is applicable to the chloride only, and a sulphate would have to be first changed into chloride by precipitation with ammonium hydroxide and re-solution in hydrochloric acid. The presence of large amounts of such salts as ammonium chloride did not aid the precipitation of the sulphate. The presence of free hydrochloric acid must be avoided and it is best to use a fresh solution of sulphurous acid or the sulphur dioxide gas direct.

This method affords an excellent means of separating zirconium from iron. Several experiments were carried out upon solutions containing known amounts of the chlorides of these two metals. The zirconia was precipitated by sulphurous acid, boiled five minutes, and washed four or five times with hot water. The iron was titrated in the filtrate.

The experiments resulted as follows:

| | Found. | Used. |
|------------------------|--------|--------|
| ZrO ₂ | 0.1074 | 0.1070 |
| Fe..... | 0.0825 | 0.0823 |
| ZrO ₂ | 0.1078 | 0.1070 |
| Fe..... | 0.0820 | 0.0823 |
| ZrO ₂ | 0.1043 | 0.1043 |
| Fe..... | 0.0439 | 0.0423 |

This method served for the separation of zirconium and aluminum as well, as may be seen by the following results:

| | Found. | Used. |
|--------------------------------------|--------|--------|
| ZrO ₂ | 0.1042 | 0.1043 |
| Al ₂ O ₃ | 0.0608 | 0.0610 |
| ZrO ₂ | 0.1070 | 0.1070 |
| Al ₂ O ₃ | 0.0316 | 0.0305 |

ON THE ANALYTICAL PROPERTIES OF IRON PHOSPHIDE AND PHOSPHATE.

BY L. M. DENNIS AND B. S. CUSHMAN.

Received May 17, 1894.

IN the year 1886, Cheever, in an article in the *Transactions of the American Institute of Mining Engineers*, 15, 448, sought to explain the variation in effect of a definite amount of phosphorus upon the properties of iron and steel by assuming that the phosphorus exists in the metal in two conditions; *viz.*, as phosphide, which is harmful, and as phosphate, which is harmless, or comparatively so. To demonstrate this he used the following method:

"A weighed sample of iron is treated in the cold with a solution of the double chloride of copper and ammonium until the iron is all dissolved, then filtered without washing. The residue of copper, carbon, phosphorus, etc., is next digested at 50° C. for two hours with 100 cc. of a saturated solution of ammonium oxalate, then filtered and washed; the filtrate contains the phosphate of iron; the residue the phosphide."

Later, in the same article, he shortens the method as follows:

"The copper, carbon, phosphorus, etc., residue is shaken in a flask for five minutes with seventy-five cc. of a cold, one per cent. solution of hydrochloric acid (two cc. strong hydrochloric acid to 100 cc. water—free from chlorine), then filtered and washed with water, the filtrate made strongly acid with nitric acid and evaporated nearly to dryness, and the phosphorus precipitated by molybdate solution."

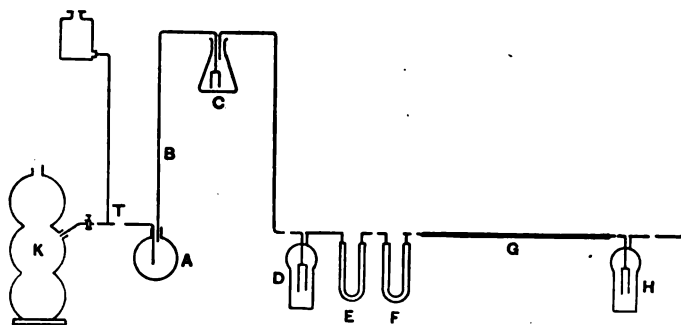
In a second paper in the same Journal, 16, 269, Cheever gives results obtained by another method, he here volatilizing the iron as chloride by chlorine, "and analyzing the residue for phosphorus, which, if present, must be in the form of phosphoric acid; for the iron phosphide would be volatilized."

At that time doubt was cast upon the accuracy of Cheever's work because of the uncertainty as to the behavior of phosphide of iron towards the different reagents which he employed. In the hope of removing some of that uncertainty the authors entered upon the experimental work detailed below.

Preliminary work upon the phosphides of iron carried out by Mr. Russell Elliott in this laboratory in 1891-2, seemed to show that the different phosphides, of which, according to Freese,¹ there are three, Fe_3P , FeP , and Fe_2P , behave quite similarly towards various solvents. For this reason, and also because of the length of time required for the preparation of a pure sample, we prepared and examined only one of the phosphides, selecting that which is formed by treating anhydrous ferrous chloride with phosphine at a red heat.

Ferrous Chloride.—The purest piano wire obtainable was placed in a combustion tube, which was connected on one side with an apparatus furnishing dry hydrochloric acid gas, and on the other side with a Schiff nitrometer² filled with strong potassium hydroxide solution. When the air in the tube had been completely displaced by the hydrochloric acid gas, as was shown by the complete absorption of the gas by the caustic potash solution, the combustion tube was heated to redness. The ferrous chloride produced was partly in the form of glistening light-yellow plates, and partly a yellowish amorphous powder. Careful tests showed that it was completely free from ferric chloride.

Phosphine.—The phosphine was generated by the action of a solution of potassium hydroxide upon phosphorus. The form of apparatus finally adopted has given such satisfactory results that a brief description of it may not be out of place. It consists of:



1. The 500 cc. distilling flask A in which the phosphine is generated.

¹ *Pogg. Ann.*, 132, 225.

² *Ztschr. anal. Chem.*, 7, 430.

2. The upright tube B which serves as a condenser, and which is widened after entering the cooling flask C to prevent its becoming clogged by the condensation of the phosphorus.
3. The cooling flask C which is surrounded with ice-water.
4. The wash-bottle D.
5. The two U tubes, E and F, filled with calcium chloride for drying the gas.
6. The combustion tube G.
7. The wash-bottle H which prevents the air from diffusing back into the combustion tube.
8. A Kipp apparatus, K, for generating hydrogen.
9. The J tube T, through which water could be driven into A from the reservoir above in order to stop the generation of the phosphine by diluting the caustic potash solution.

The most uniform evolution of phosphine was obtained by using a 1 : 1 solution of potassium hydroxide, a stronger solution causing a more rapid generation of the gas than was desirable. Although the phosphine resulting from the use of this moderately concentrated caustic potash was not as pure as that obtained with a very concentrated solution,¹ yet the phosphide obtained was probably not influenced to any great extent by the small amounts of hydrogen given off early in the phosphine evolution. The hydrogen would reduce some of the ferrous chloride to metallic iron, but if we accept the statement of Freese,² the product is the same whether phosphine acts upon anhydrous ferrous chloride or upon metallic iron. To avoid, however, the production of any unnecessarily large amount of hydrogen the contents of the generating flask was at no time heated to boiling, this precaution serving to lessen the amount of hydrogen arising from the secondary reaction between the potassium hydroxide and potassium hypophosphite:



It was thought that the hydrogen thus set free might reduce the phosphide after the latter had formed, but later experiments with the pure phosphide showed that it was not reduced when highly heated in a current of hydrogen. The solution of potassium hydroxide should be cooled before being poured upon the

¹ A. W. Hofmann, *Ber. d. Chem. Ges.*, 1871, 200.

² *Pogg. Ann.*, 132, 225.

phosphorus in the flask, in order to avoid the immediate generation of any phosphine, as that would cause an explosion upon coming in contact with the air in the flask. As soon as all connections had been made, hydrogen from the Kipp generator was run through the apparatus until all air had been expelled. The sand-bath under the generating flask was then gently heated until the phosphine began to come off somewhat rapidly. The hydrogen was then shut off and the flame removed, the latter being replaced only when the solution of the gas had nearly ceased. This procedure greatly lengthened the duration of the current of phosphine.

When nearly all of the hydrogen had been driven from the apparatus the phosphine burst into flame at the end of the outlet tube. The combustion tube was then heated. As soon as the hydrochloric acid gas, formed by the action of the phosphine upon the ferrous chloride, began to come off, the flame at the outlet tube ceased to burn. The ferrous chloride gradually darkened, and after half an hour, when the reaction was completed, it had assumed a dark bluish-gray color.

Upon breaking the tube there was found a brittle, porous substance which rarely showed any crystalline structure. It was powdered in an agate mortar, then digested with hot hydrochloric acid (1:12) until it was not at all attracted by the magnet, and was finally dried over sulphuric acid in an atmosphere of carbon dioxide.

Analysis of the Phosphide.—Stöckmann¹ states that he always obtained too low results for phosphorus when aqua regia was used as a solvent for spiegeleisen. He also tested the gases which were given off when the sample was dissolved, by passing them through an oxidizing medium, and in each case was able to detect phosphorus in them. For this reason we first tried other solvents, but although the phosphide was quite strongly attacked by nitric acid and by hydrochloric acid, and especially by nitric acid to which potassium chlorate was gradually added in small amounts, complete solution was in no case effected even by several hours treatment.

Portions of the phosphide were then treated with aqua regia in a small flask to which a return-flow condenser was attached.

¹ *Ztschr. anal. Chem.*, 16, 175.

After passing through the condenser the escaping gases were passed through a Mitscherlich bulb containing a solution of potassium hydroxide which had previously been saturated by chlorine. After the phosphide had been completely dissolved, the potassium hydroxide solution was acidified with nitric acid and was repeatedly evaporated with nitric acid until all chlorine had been expelled. Ammonium molybdate was then added, but no trace of a precipitate resulted. Aqua regia was, therefore, adopted as the solvent for the phosphide.

The following method of analysis was first tried :

About 0.1 gram of the phosphide was dissolved in aqua regia (one part of nitric acid to three parts of hydrochloric acid), and the solution, after being diluted, was precipitated by ammonium hydroxide. An excess of ammonium sulphide was then added to break down the ferric phosphate, and the solution was kept at 70° C. for fifteen hours. The ferrous sulphide was then filtered off, dissolved in dilute hydrochloric acid, and the iron then oxidized by bromine water. Upon precipitating this solution with ammonium hydroxide and weighing the iron as ferric oxide, too high results were obtained since the precipitate was found to contain phosphoric acid.

The method finally adopted for the analysis of the phosphide was as follows :

The sample was dissolved in aqua regia, the solution repeatedly evaporated with nitric acid, and the phosphoric acid determined by the molybdate-magnesia method. To determine the iron in the filtrate from the ammonium phosphomolybdate precipitate, the method of W. H. Krug¹ was used with satisfactory results. The iron was precipitated in the cold with ammonium hydroxide, and the ferric hydroxide, after thorough washing, was dissolved in nitric acid and again precipitated from the cold solution with ammonium hydroxide. After washing until all chlorides had been removed, the iron was weighed as Fe_2O_3 .

The results obtained were as follows :

| | Found. | Calculated for | |
|----------|--------|-------------------------|--------------|
| | | Fe_3P_4 | FeP |
| Fe | 64.21 | 57.52 | 64.36 |
| P | 35.62 | 42.48 | 35.64 |

¹*J. Anal. Appl. Chem.*, 5, 674.

The work of other investigators in this field had led us to expect as a product, not FeP but Fe_3P_4 . Yet the constancy of composition shown by separately prepared portions of our product, its completely non-magnetic character and the agreement of the analysis with the calculated percentages, leave but little doubt as to the purity and identity of the phosphide.

The fact that the true phosphides of iron are *non-magnetic* seems to have been overlooked by recent writers, a circumstance which has probably led Hvoslef, Schneider, Percy, and others, to regard a mixture of phosphide of iron and iron (they give it the formula Fe_3P) as a definite phosphide. Howe¹ cites the work of Hvoslef and Percy, and says: "These facts suggest that iron and phosphorus preferentially combine in this particular ratio." But he does not mention the careful and extended researches of Freese upon this subject, who says:² "Endlich habe ich versucht, das von Hvoslef beschriebene Phosphoreisen Fe_3P , welches derselbe durch Glühen des Phosphorets FeP unter einer Decke von Borax erhalten haben will, darzustellen, allein bis jetzt vergeblich." After describing some of his own experiments, made according to Hvoslef's method, Freese concludes: "Hieraus schliesse ich, dass Hvoslef's Phosphoreisen nur ein Gemenge von Eisen mit Phosphoreisen ist, denn stets fand ich bei einem anerkannt reinen Eisenphosphoret den nach längerer Behandlung mit heisser Chlorwasserstoff säure verbliebenen Rückstand mit dem Phosphoret gleich zusammengesetzt."

Ferric Pyrophosphate.—This salt was chosen as representing perhaps more nearly than any other the condition of the oxidized phosphorus in iron and steel. A sample of the pure ferric pyrophosphate was heated for half an hour over the full Bunsen flame: it retained its yellow color and was completely soluble in concentrated hydrochloric acid.

Experiments with Solvents.—Before attempting to separate the phosphide of iron from the pyrophosphate in samples of iron or steel, it was necessary to find a solvent which would completely dissolve the pyrophosphate and leave the phosphide unattacked. The reagents tried were solutions of ammonium oxalate, potassium oxalate, ammonium citrate, ammonium carbonate, ammo-

¹ Metallurgy of Steel, p. 55.

² Pogg. Ann., 132, 262.

nium cupric chloride, and dilute solutions of chromic, sulphuric, nitric, and hydrochloric acids; both rapid boiling and long digestion at 100° C. were employed. Clear solutions of the pyrophosphate were obtained only with ammonium oxalate, ammonium citrate, and hydrochloric acid. Portions of fifty milligrams of the pyrophosphate were then digested on a hot plate with 100 cc. of each of these three solvents. Complete solution resulted

| | |
|-------------------------------------|--------------|
| with hydrochloric acid (1:1)..... | in 2 minutes |
| “ ammonium oxalate (concentrated).. | “ 45 “ |
| “ “ citrate (sp. gr. 1.09) | “ 90 “ |

On diluting the ammonium oxalate solution with water a white precipitate resulted, and as this could be dissolved only by adding hydrochloric acid and boiling, the use of ammonium oxalate was abandoned.

One hundred milligram portions of the phosphide were then treated with hydrochloric acid and ammonium citrate under the same conditions as were required for the complete solution of the pyrophosphate. The residues were collected on counterpoised filters, dried, and weighed. It was found that the phosphide which had been digested with hydrochloric acid had lost about four per cent. of its weight. The filtrate from this portion, after the hydrochloric acid had been expelled by evaporation with nitric acid, gave strong tests for both iron and phosphorus. The sample of phosphide which had been digested with ammonium citrate showed no appreciable loss of weight, and hence a solution of this reagent, of a sp. gr. of 1.09, was used in the following experiments upon the separation of the pyrophosphate of iron, and phosphide of iron, in samples of iron and steel.

Before trying the ammonium citrate solution a preliminary experiment was made to ascertain the nature of the action of hydrochloric acid (1:1) upon the phosphorus in iron. A sample of pig iron, containing 0.205 per cent. total phosphorus, was treated with the acid until all action had ceased. The solution was filtered, the filtrate evaporated with nitric acid, and the phosphorus determined by the molybdate-magnesia method. Two determinations gave 0.153 and 0.154 per cent. phosphorus. The determination of the phosphorus in the unattacked residue showed that only 0.008 per cent. remained behind, from which

it follows that over twenty per cent. of the phosphorus present escaped in gaseous form during the solution of the iron.

The ammonium citrate separation was then tried on two samples of steel to ascertain whether the method would give agreeing results. The sample should be as finely divided as possible, and for this reason filings were used in the following determinations:

Five grams of "Open Hearth" steel was digested on a hot plate (100°), with ammonium citrate solution, for an hour and a half. The solution was then filtered through asbestos. The residue was thoroughly washed with water, dissolved in nitric acid (1.20 sp. gr.), and the phosphorus determined by the molybdate-magnesia method.

Total phosphorus in the sample was 0.044 per cent.

Phosphorus in the residue after treatment with ammonium citrate, 0.033 and 0.032 per cent.

A sample of Bessemer steel, containing 0.107 per cent. total phosphorus, gave by the same method 0.046 and 0.053 per cent. of phosphorus in the residue.

No further analyses of iron or steel samples were made, for our object in taking up the work was not the investigation of the condition of phosphorus in samples of commercial products, but was merely to attempt to devise a method to separate phosphide of iron from pyrophosphate.

The chlorine method employed by Cheever was also tried on the phosphide and pyrophosphate.

Eighty milligrams of the phosphide were heated in a current of dry chlorine. As the temperature rose sparks shot out from the surface of the phosphide. At a low red heat a glow ran through the substance which then melted and volatilized completely in a few minutes.

A sample of the ferric pyrophosphate was then heated for half an hour in a current of chlorine at the highest temperature obtainable by the use of a combustion furnace, but no loss in weight resulted.

A mixture of 0.0435 gram of the pyrophosphate, with 0.0292 gram of the phosphide, was then heated in chlorine in the same manner. The residue in the boat weighed only 0.0231 gram. As this seemed to indicate that in the volatilization the phos-

phide exerts some reducing action on the pyrophosphate, causing a volatilization of some of the constituents of the latter compound, another experiment was tried with a mixture containing a slightly higher per cent. of phosphide, to see whether there would be a correspondingly greater loss in the pyrophosphate.

0.0561 gram of the pyrophosphate, and 0.0472 gram of the phosphide, treated with chlorine, gave a residue weighing 0.0193 gram, a result which seems to sustain the above supposition.

CORNELL UNIVERSITY,
May, 1894.

NOTES ON ALUMINUM.¹

BY GEORGE FREDERICK ANDREWS.

THE writer of this paper has made a large number of experiments with aluminum particularly with reference to its use in jewelry etc. The facts stated are the results of some of these experiments.

Alloys containing Gold.—The alloys of gold and aluminum are interesting, though of little practical use except for decorative purposes. The alloy with six per cent. of gold is as white as pure aluminum but much more brittle. The alloy with ten per cent. of gold is harder than aluminum but does not work well, except at a high temperature. Its color is light violet-brown. The alloy with fifteen per cent. of gold is a very soft fine-grained metal. It has a slight violet tint, although nearly white. The alloy with fifty per cent. of gold has a beautiful violet color. It is very soft and spongy. The alloy with seventy-eight per cent. of gold is very brittle. The color is peculiar; it is between pink and violet. The alloy with ninety per cent. of gold has a pale violet color, while the alloy with ninety-four per cent. of gold has a color approaching pink again. Alloys containing small percentages of aluminum leave a bright violet color on the cupel, under the blowpipe.

An alloy containing fifty per cent. of gold, forty-five per cent. of copper, and five per cent. of aluminum takes the color and polish of fourteen carat gold but easily tarnishes. This alloy has also been used in electroplating, but it is not entirely satisfactory for this purpose.

Alloys containing Silver.—Alloys containing from four to eight

¹ Abstract from a paper read before the Rhode Island Section, February 15, 1894.

per cent. of silver, and from ninety-six to ninety-two per cent. of aluminum are useful for many purposes. They are harder than aluminum but not brittle. They take a very fine polish and hold it well. Their color is very near that of fine silver. These alloys are now used for the manufacture of charms, medals, metal trimmings and decorations of various kinds.

Alloys containing Nickel.—The alloy containing fifty per cent. of nickel and fifty per cent. of aluminum, has a dull gray color. It is very porous and so brittle as to be useless.

The following alloys of copper, nickel and aluminum are all very hard, fine-grained and show great strength. The alloy containing sixty-six per cent. of copper, twenty-four per cent. of nickel and ten per cent. of aluminum takes a fine polish and has the color of ten carat gold. The alloy containing fifty-five per cent. of copper, thirty-three per cent. of nickel and twelve per cent. of aluminum, has a beautiful golden-brown color. The alloy containing $72\frac{1}{2}$ per cent. of copper, $21\frac{1}{4}$ per cent. of nickel and $6\frac{1}{4}$ per cent. of aluminum closely resembles it, but the color of the latter is richer and deeper. These alloys may become very useful for decorative purposes.

Solder for Aluminum.—Notwithstanding the assertions which are still heard to the contrary, aluminum can be successfully soldered. The writer has used solder which makes a clean, perfectly firm joint, and is in every way satisfactory. It requires no "soldering fluid" and no soldering iron.

Melting of Aluminum.—In melting aluminum the temperature should be kept even and not much above the melting point of the metal. The metal should be fed into the crucible in small pieces and pushed down as fast as it becomes soft. The most serviceable flux is a little tallow, although it is not necessary to use any. A sand crucible must not be used as the aluminum readily attacks the silicon.

In alloying, the aluminum should be put into the crucible after the other metal or metals have become liquid.

Restoration of the Mat.—Aluminum can be cleaned, and its peculiar mat restored by dipping for a minute and a quarter, in a solution of three ounces of caustic potash in a quart of water, then washing thoroughly and dipping in a mixture of three parts nitric, and two parts sulphuric acid, by volume.

Caustic soda can be used with nearly as good results. The main advantage in the substitution is the lower price of caustic soda.

LABORATORY OF CORNELL AND ANDREWS.

PYROXYLIN, ITS MANUFACTURE AND APPLICATIONS.

BY WALTER D. FIELD.

(Continued from Vol. 15, p. 140.)

Received September 12, 1893.

PART II.

NITRATION OF THE FIBER.

MIXED cotton and flax fiber in the form of paper, from two to three one-thousandths of an inch thick and cut into one inch squares, is nitrated by the Celluloid Manufacturing Company, and the same paper, left in long strips, one inch wide, is used for nitration by the Zylonite Manufacturing Company, of North Adams, Mass. The Celluloid Manufacturing Company introduce the cut paper into the mixed acid by means of the arrangement shown in Fig. 1, H, which is a rapidly revolving,

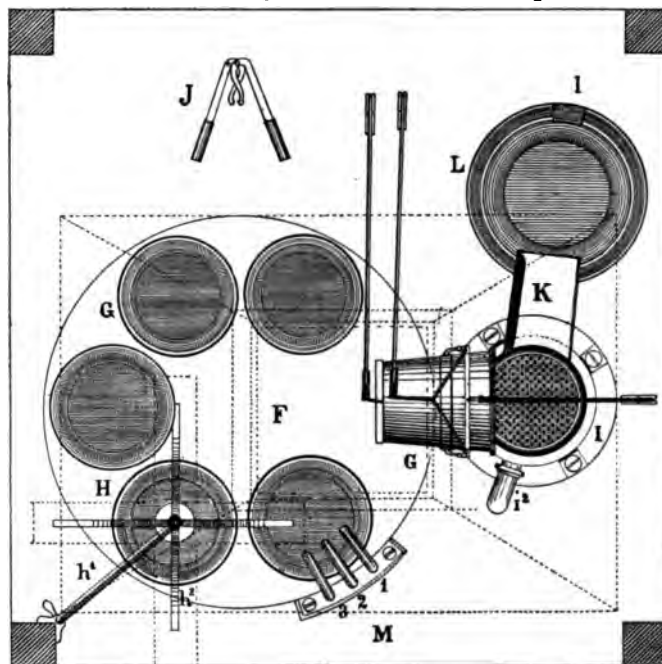


FIG. 1.

in Fig. 3. It is sufficient in size to nitrate one pound of cotton.

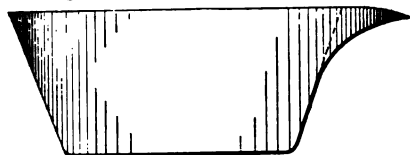


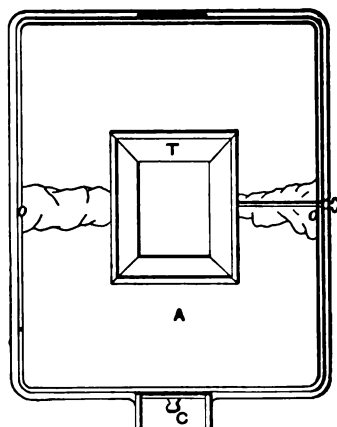
FIG. 3.

The hook on one end of the rod enables the workmen to pull the pyroxylin apart and thus insures saturation of the fiber.

The nitrating apparatus of Tribouillet and de Besaucele

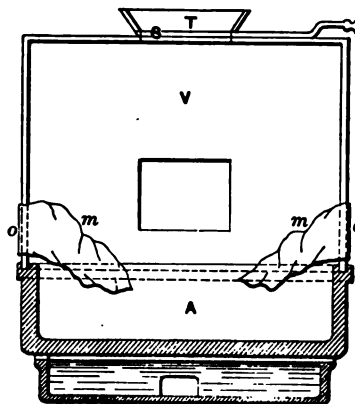
(Eng. Pat., No. 5,057, 1878; Ger. Pat., No. 6,828, 1879) is given by both Bockman (*Das Celluloid*, 1888) and Heinzerling (*Die Fabrikation Kautschuk and Guttapercha Waaren*, 1883), and it is the only apparatus they mention, although Hyatt's apparatus was then in use. The plans for this nitrating box have been reproduced in Figs. 4 and 5. It is of a very unhandy construction and any workman using it would soon discard the hood V as unnecessary. The rubber sleeves would only be in his way and the acid would rot them out in a very short time.

FIG. 4.



PLAN.

FIG. 5.



SECTION.

In working by hand, at the present time, it is customary to protect the workmen from the fumes of the acid by means of a hood which is being constantly exhausted by a powerful fan or blower. They are furnished with gauntlet gloves made of white rubber, and also aprons of the same material. In the winter season the room in which the nitrating is done must be kept at a tem-

perature of about 70° F., in order to secure equality in the batches.

The nitrating apparatus of White and Schupphous (U. S. P., No. 418,237, 1889) is both novel and excellent in its general plan. The cage B (Fig. 6), with its central perforated cylinder B' (Fig. 7), is intended to insure the rapid and perfect saturation

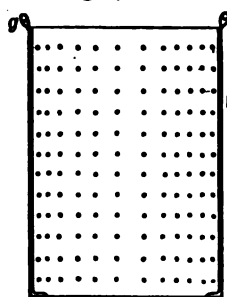


FIG. 6.

of the tissue paper used for nitrating. The patentees say that no stirring is required with their apparatus. This might be true when paper is used, or even cotton, when the temperature of nitration is from 30° to 35° C., but would not be true if the temperature were

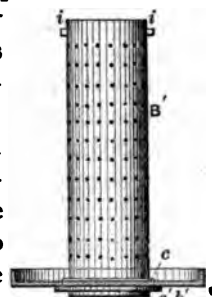


FIG. 7.

raised to 50° or 55° C. In carrying out their process they proceed as follows: The paper is nitrated in the cage B, the bottom of which is formed by the flanged plate *c* fastened to the bottom of the internal cylinder B'. After nitration the cage is carried to the wringer E, Fig. 8, of which it forms the

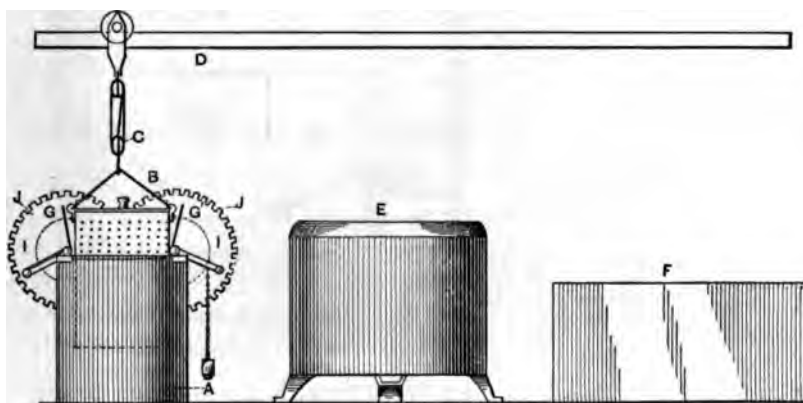


FIG. 8.

basket, and the acids removed. Finally the cage is taken to the plunge tank F where the paper is removed from the cage by simply pulling out the central perforated cylinder B'. Fig. 9, shows the nitrating pot with its automatic cover. The plunge tank F is shown in section and plan in Fig. 10. This appara-

tus is given in detail because it is the only patented method that seems to be suitable for the nitration of cotton fiber in bulk at high or low temperatures.

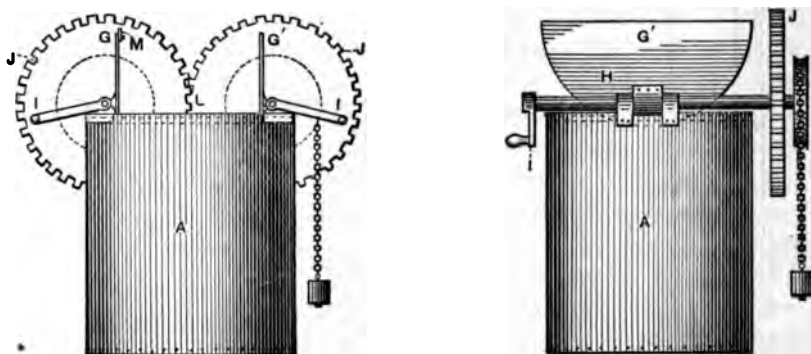


FIG. 9.

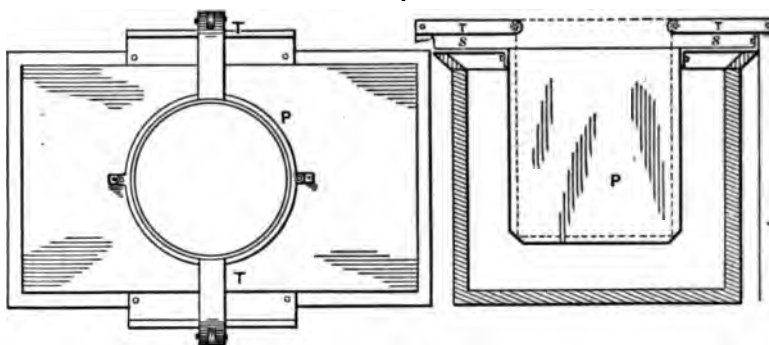


FIG. 10.

We now come to what is probably the most elaborate method of nitrating yet suggested—that is, the method patented by Mowbray, August 12, 1890 (U. S. P., No. 434,287), by which he proposes to nitrate paper in continuous lengths. The method is as yet untried. The paper loops shown in the sectional drawing (Fig. 11) are merely theoretical, for the paper web would not maintain any such position, but would settle down in the bottom of the acid tank. He allows the paper web to remain in the nitrating, or acid tank (15), from twelve to twenty minutes, then as the first part of the paper web is drawn forward, a fresh portion takes its place. One of the great problems in such an operation is how to maintain the strength of acid required in the nitrating

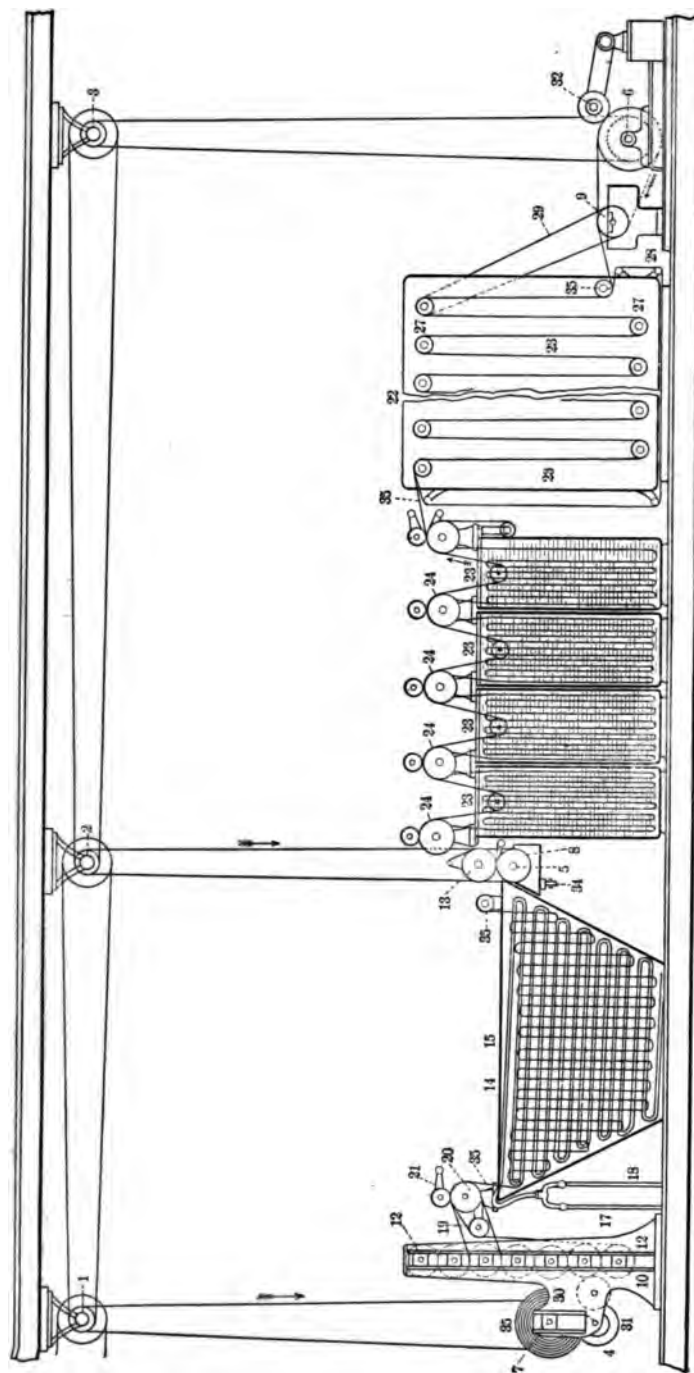


FIG. 11.

tank. Mowbray claims to be able to do this by using the methods described by him in U. S. P., Nos. 350,497, and 350,498. Such a method as Mowbray describes is certainly no better than that of Hyatt (210,611).

The best material from which to construct the various tanks required for storing the acids for nitrating vessels and for other things is, undoubtedly, steel. Mowbray, in his patent No. 350,489, 1886, claims "the use of homogeneous metal, otherwise called 'Bessemer steel' plates, for tanks, to serve as containing vessels for the mixed acids used in the process of converting cellulose into nitrocellulose." He also claims "the use of steeled cast-iron pots for holding the mixed acids, in which the cellulose is immersed during the process of conversion." Mowbray says, in the same patent: "I have discovered that cast-iron vessels treated so as to diminish the carbon therein (by exposure to continued heating, surrounded by infusoria, or iron peroxide), can be successfully used for this purpose, and that the action of acids upon metals forms a ferric sulphate which, being insoluble in the mixed nitric and sulphuric acid used, does not injuriously affect the product."

One way of constructing the vessel for holding the waste acids from the nitrating pots can be seen in Fig. 12. The inside vessel,

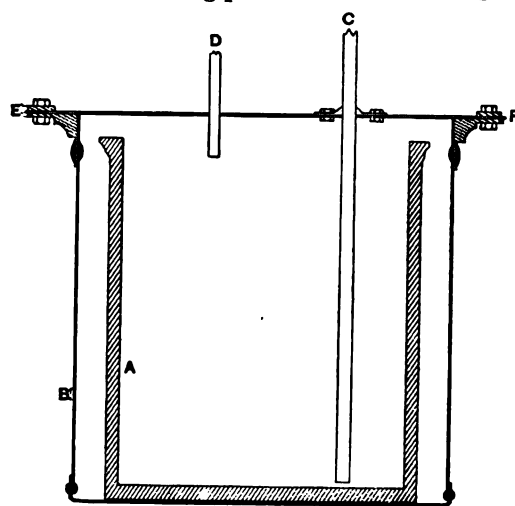


FIG. 12.

A, is of earthenware, and may have a capacity of from 100 to 500 gallons, according to necessity. The outside vessel is of boiler steel with a flanged top, E, F. The pipe D is connected with the compressed air, and the pipe C conducts the acid as it is forced out to the desired place. It is a construction that

prevents any accidents when moving the acids from place to place.

Hyatt, in U. S. P., No. 299,388, a patent for a combination of tanks so arranged as to allow of the convenient handling of the mixed acids, simply says in regard to the construction of the tanks: "We prefer to construct our tanks of wrought iron, and protect them from the corrosive action of the acids by acid-proof coatings." Steel drums will hold the mixed acids so long as they are closed from the air, but if air is allowed to enter, the sulphuric acid in the mixed acids takes up the moisture in the air, are reduced in strength at the surface, and soon begin to eat the iron or steel away. There is some choice, perhaps, in the steel to be used for such a purpose, but wrought iron is as good as steel if the air is carefully excluded from the tank. All the plants and arrangements of tanks, etc., both for nitrating and storing and using the waste acids, have been designed for an acid mixture having about the following strength:

| | | |
|----------------------|----|-------------------|
| Sulphuric acid | 66 | parts (absolute). |
| Nitric acid | 17 | " " |
| Water | 17 | " " |

the acids being used at a temperature of 30° C.

The arrangement of the plant, as described by Mowbray in U. S. P., No. 350,496, or the arrangement described in U. S. P., No. 299,388, by Hyatt, Pool, Everding, Stevens, and Wood, could not be used were the acid mixture in use of the following composition:

| | | |
|----------------------|----|-------------------|
| Sulphuric acid | 62 | parts (absolute). |
| Nitric acid | 24 | " " |
| Water | 14 | " " |

and using a temperature of 60° C. for immersion.

The nitrating apparatus of Schupphous, Mowbray, and Hyatt, were all designed for use with tissue paper as the cellulose material. The design of Schupphous might be used for cotton at low temperatures, but would be inconvenient on account of the length of time (five or six hours) required for nitrating at low temperatures.

Thus it is apparent that both the cellulose material and the method of nitrating control the construction of the nitrating plant. No plant has yet been designed for nitrating cotton fiber in its natural form at high temperatures, and using more than one pound of cotton at an immersion.

The Acid Mixture.—Many formulas have been published for producing soluble nitrocellulose. Few of them give detail enough to make them available for practical working. In many instances, although the observations were correct for the single experiment, a dozen experiments would have produced a dozen different products. Some formulas give no temperature for the immersion, others neglect even to give any specific gravities for the acids, and rather than attempt to utilize any published formula, it would be much better to spend months working out a new one to one's own satisfaction and instruction.

In the last five years, the manufacture of a pyroxylin that is almost the equivalent of the collodion cotton, has enormously increased, by reason of its use in the manufacture of pyroxylin varnishes and transparent films for photographic plates.

At the present time not more than three different formulas are in use by the manufacturers of soluble nitrocellulose in this country. The one used by the celluloid manufacturers, another in which the cotton is nitrated at high temperatures, and a third in which the temperature of the immersion is low and the time of the nitration about six hours. Of the three, the best method is the last one, or the one in which the cotton is immersed at a low temperature and then the reaction allowed to proceed in pots holding from five to ten pounds of cotton.

The following formula is essentially the one in use by the celluloid manufacturers for the production of the low form of nitrated product which they use:

| | | | | |
|---------------------|----|-------|----|---------|
| Sulphuric acid..... | 66 | parts | by | weight. |
| Nitric acid | 17 | " | " | " |
| Water | 17 | " | " | " |

Temperature of the acids at the immersion, 30° C., and the time of the immersion from twenty to thirty minutes. Cellulose in the form of tissue paper about two one-thousandths of an inch thick, one pound to 100 of acid mixture.

The nitrocellulose produced by this formula is very insoluble in the compound ethers and other solvents of pyroxylin, and is seemingly only converted or gelatinized by the action of the solvent.

The next formula produces a mixture of tetra- and penta-nitrocelluloses, hardly soluble in methyl alcohol (free from

acetone), but very soluble in anhydrous compound ethers, ketones, and aldehydes.

Nitric acid, sp. gr., 1.435 8 pounds.

Sulphuric acid, sp. gr., 1.83..... 15½ "

Cotton, fourteen ounces, temperature of immersion, 60° C. Time of the immersion, about forty-five minutes. The 60° of temperature is developed by mixing the acids together. The cotton is allowed to remain in the acid until it feels "short" to the rod.

We have here the temperature record for a single batch, (made in the form of bowl given in Fig. 1) during the time of the nitration. From four to five minutes were required to immerse the fourteen ounces of cotton and then the acids had risen in temperature from 60° to 65° C. In ten minutes the temperature in the upper part of the bowl was 63½° C., and in the bottom 66° C. The batch was then turned over in the bowl and in another ten minutes the temperature of the top of the cotton was 59° C., and in the bottom 62° C.

At the end of thirty minutes the temperature of the top was still 59° C., and the bottom 60° C. During the remaining hour and ten minutes the temperature of the top of the acid ranged from 53° to 56° C., and from 64° to 67° C. in the bottom. The time of the immersion was one hour and forty minutes. The pyroxylin produced in this immersion was not a very soluble one, quite a large proportion being insoluble in compound ethers. It will be noticed that there were two periods in which the temperature in the batch rose, and two distinct reactions took place. If the temperature during the first thirty minutes has gone up to 70° C., or 4° higher than it did go, the cotton would have been finished inside of forty-five minutes, and the pyroxylin produced would have been perfectly soluble in compound anhydrous ethers. These observations have been verified a large number of times.

The table given below is a careful record which plainly shows the great variation in the time of the immersion and the temperature by seemingly very slight causes. The table extends over fourteen working days, during which time it rained four days. The formula used is that last given, except that the

specific gravity of the nitric acid is somewhat lower. The pyroxylin produced differs only from that produced by using a nitric acid of sp. gr. 1.43, in being soluble in methyl alcohol. From thirty to thirty-five pounds of pyroxylin were produced in each of the fourteen days.

| Weather. | Specific gravity. | | Time. | | | | Temperature, degrees C. | | Percent-age. | |
|-----------------------|-------------------|---------|--------|----------|--------|----------|-------------------------|-----|--------------|-------|
| | Sul-phuric. | Nitric. | Hours. | Minutes. | Hours. | Minutes. | From. | To. | Increase. | Loss. |
| 1. Clear | 1.8380 | 1.4249 | .. | 20 | 4 | .. | 57° | 62° | 31 | .. |
| 2. " | 1.837 | 1.4249 | .. | 20 | 3 | .. | 60° | 62° | 18 | .. |
| 3. Cloudy | 1.837 | 1.4226 | .. | 45 | 3 | .. | 60° | 62° | 7 | .. |
| 4. Rain | 1.837 | 1.4200 | .. | 20 | 1 | 20 | 60° | 63° | 0 | 0 |
| 5. Clear | 1.8377 | 1.42 | 1 | 15 | 2 | .. | 58° | 62° | 15 | .. |
| 6. Rainy | 1.8391 | 1.422 | .. | 35 | 1 | 40 | 58° | 62° | .. | 2 |
| 7. Cloudy | 1.835 | 1.4226 | .. | 20 | .. | 35 | 62° | 64° | .. | 10 |
| 8. Clear | 1.835 | 1.4222 | .. | 35 | 1 | 10 | 60° | 62° | 5 | .. |
| 9. Partly clear..... | 1.824 | 1.4271 | .. | 20 | 1 | .. | 50° | 60° | .. | 3 |
| 10. " | 1.83 | 1.4271 | .. | 10 | .. | 25 | 58° | 60° | .. | 10 |
| 11. Cloudy | 1.832 | 1.425 | .. | 10 | .. | 50 | 58° | 60° | 8 | .. |
| 12. Rainy | 1.822 | 1.425 | .. | 10 | .. | 20 | 58° | 60° | .. | 10 |
| 13. Partly clear..... | 1.8378 | 1.4257 | .. | 50 | 1 | 40 | 50° | 58° | 20 | .. |
| 14. Cloudy | 1.837 | 1.4257 | 1 | 56 | 4 | 40 | 50° | 60° | 16 | .. |

A careful examination of this table will prove very instructive. The increase in yield varies from thirty-one per cent. to nothing, and the loss runs as high as ten per cent., yet it would be unjust to say that care was not taken to make the product uniform in quality.

On the days it rained there was a loss, with the exception of the fourth day when there was neither a loss nor a gain. On the days it was partly clear, as just before or after a rain, the table shows a loss in product. We can explain this fact by reason of the moisture-absorbing qualities of the cotton. On the rainy days it would absorb the moisture from the air until, when immersed in the acids, they were weakened, and the fiber dissolved more or less in the weakened acid, producing what is known as "burning" in the batch. It will also be noticed that on the days which show a loss, the time of the immersion was correspondingly short, as on the tenth, twelfth, and seventh days.

The lesson this table teaches is, that it is almost impossible to nitrate cellulose in small quantity and get uniform results when the nitration is carried on at high temperatures.

In the next table we have the condensed results from a month's work with the above formula.

| | |
|---|-----------------------|
| Cotton (scoured, upland)..... | 416 pounds, 12 ounces |
| Nitric acid, sp. gr. 1.42-1.425 water white | 4,957 " |
| Sulphuric acid, sp. gr. 1.83-1.837 | 9,803 " |
| Product | 513 " 6 ounces |

The high temperature nitrating formula taken as the example in this article will be found to lead to a correct judgment of the working of all such formulas. The consideration of the cold nitration method I shall make the subject of a separate paper at some later date.

IMPROVEMENTS IN THE MANUFACTURE OF SULPHURIC ACID.

BY PETER S. GILCHRIST.

Received May 14, 1894.

IN the JOURNAL for November, 1893, I gave a brief outline of the Hacker and Gilchrist pipe columns for saving chamber space, quoting results which had then been obtained in actual working. I wish to follow this with results of much greater interest.

As stated previously, the pipe columns were added to a plant having large chambers, the first three being each 160 feet long, and consequently not so effective as in combination with short chambers, the best work being seventeen cubic feet of chamber space per one pound of sulphur per twenty-four hours, and this with Glover and Gay-Lussac towers. The ratio of chambers have an important bearing on the amount of work done in a given space.

It has long been thought that short chambers were essential to good work, repeated experiments in Europe having demonstrated this, but there has been much tardiness in adopting them.

An observer of the chamber process notices that as the gases pass from one chamber to another a greater reaction sets in, consequently followed by an increased production of sulphuric acid. The reasons for this are obvious; the vapors strike against the surfaces of the chamber ends and the sides of the connection, causing the particles forming to interact more quickly. Again,

the gases being passed through a small aperture become better mixed, and the gases are also cooled by radiation from the lead surfaces, which is an important point in manufacturing. It has been proved in chambers of 100 feet and over, that after the gases have traversed fifty to fifty-five feet of the length the acid produced falls off considerably, so by cutting off the chamber at this point we get the maximum work from the chamber.

The important point in constructing a sulphuric acid plant is to endeavor to attain these conditions throughout the process as much as is possible, and if the mere passage of the gases from one chamber to another have such visible effects, how much more so, when these conditions are very greatly improved on, as is the case when using pipe columns.

The large, moist surfaces presented by the numerous pipes upon which the gases impinge, the thorough mixing which the gases receive by coming in contact with each successive layer of pipes, and lastly, the heat generated by the reaction, consequent upon the mixing, being carried off by the cold air passing through the pipes, are conducive to a very rapid formation of sulphuric acid.

The cyclone of last August having destroyed the acid chambers of the Darlington Phosphate Company, of Darlington, S. C., I was asked to superintend the rebuilding of the same.

The original plant consisted of three chambers, having a total capacity of 129,500 cubic feet, with a small coke tower in the rear, using Johnson's mechanical fines-furnaces, with no niter recovery, making at the outside eleven tons of 50° Beaumé acid per day.

The present plant consists of four small chambers, the first only fifteen feet long, its object being to catch the dust, the second sixty feet, the third fifty feet, and the fourth forty-three feet, having a total capacity of 100,800 cubic feet, with coke tower in the rear, using the same furnaces, and no niter recovery.

Between each chamber there is a pipe column averaging 3'.10" by 3'.5", and 13'.6" high, between the last chamber and the coke tower, a small pipe case 3'.0" by 1'.10", and 6'.0" long.

The average work for the last eighty-one days is as follows: Pyrites burned per day, 14,304 pounds, averaging 44.6 per cent.

sulphur, two-thirds being Virginian ore, and one-third Spanish, actually yielding forty-three per cent. sulphur. This is an equivalent of 6,153 pounds of sulphur, being 16.38 cubic feet of chamber space, per one pound of sulphur, per twenty-four hours, and in the cooler months was under fifteen cubic feet.

The average yield of acid for this period was fourteen tons of 50° Beaumé acid per day, or 4.552 pounds of 50° acid, per one pound of sulphur, per twenty-four hours.

As this means an increase over the total chamber area of seven-tenths of an inch, calculated as 50° acid, one can readily appreciate the amount of work done in the system.

The average temperatures of the chambers were as follows:

| No. of chamber. | Front. | Back. |
|-----------------|---------|---------|
| 1..... | 220° F. | 222° F. |
| 2..... | 178° " | 176° " |
| 3..... | 156° " | 154° " |
| 4..... | 123° " | 102° " |

Atmospheric temperature, 73° F. Average oxygen in the escape gases, 6.6 per cent. Average acidity in the escape gases, 0.81 grains sulphuric anhydride per cubic foot.

The result of the application of the pipe columns over the original plant is as follows: Reduction in the size of the chambers, 21.84 per cent. Increase in the yield of sulphuric acid made, 28.18 per cent. equal to a total increase of 50.02 per cent.

Another plant is being completed in Savannah, Ga., having short chambers, pipe columns, Glover, and Gay-Lussac towers, which will, doubtless, confirm more fully the advantages of the pipe columns.

SECTIONS OF PIPES.



The construction of the pipe columns have been much improved, more especially in connection with the sections of the pipes used. The exteriors are made so as to enable the greatest amount of mixing to be got from a minimum surface of contact.

NOTE ON THE DETERMINATION OF SILICA IN BLAST-FURNACE SLAG.¹

BY P. W. SHIMER, EASTON, PA.

THE object of this note is to call attention very briefly to the influence of spinel on the determination of silica in blast-furnace slags. When fluxing aluminous ores with magnesian limestone, spinel is very apt to be found in the slag, especially when the slag is basic, the alumina in this case acting as an acid and combining with part of the magnesia to form magnesium aluminate. In the determination of silica in such a slag by the method of fusion with alkaline carbonate, the spinel seems to be almost wholly unattacked by the fusion and subsequent evaporation with hydrochloric acid, and is weighed with the silica at the end of the determination. In the case of one slag, the silica, before purification, was 34.25 per cent.; after purification with sulphuric and hydrofluoric acids, it was found to be 31.52 per cent. The bluish-colored residue left after the sulphuric and hydrofluoric acid treatment was found to dissolve easily in fused potassium bisulphate, and contained alumina and magnesia in the proportions necessary to form spinel. In the case of another slag, the silica, before separation of spinel, was 39.23 per cent.; after separation, 34.73 per cent.

The points it is desired to bring out are, that spinel is not decomposed by the usual alkaline carbonate fusion and, therefore, that it is never safe to omit the treatment of the silica with sulphuric and hydrofluoric acid. All the slags in which spinel was found were stony slags and, therefore, had the usual time in which to cool and crystallize. It is quite possible that, if the same samples had been chilled, the elements of the spinel would have remained in decomposable combination with the silica. However, even in the case of chilled samples, the possible presence of minute crystals of spinel should not be ignored, especially in basic slags rich in alumina and magnesia. By successive and repeated treatment of 100 grams of a powdered spinel slag with hydrochloric and hydrofluoric acids and boiling solution of

¹Read before the Lehigh Valley Section, May 3, 1894.

sodium carbonate in a platinum dish, it was found to be possible to separate one gram of microscopic crystals of spinel quite free from all impurities.

NEW BOOKS.

"AN INTRODUCTION TO THE ORGANIC COMPOUNDS OF EVERY-DAY LIFE." BY JULIUS T. WILLARD, M. SC. 12mo. cloth, pp. IV; 203. Published by the author. Manhattan, Kansas. 1894. Price \$1.75.

Every chemist in this country feels that anything which will tend to place organic chemistry where it belongs in our Colleges and Universities should be encouraged. It was doubtless this feeling which prompted the author to publish this little volume. The book is indeed what it pretends to be, a simple compilation. The arrangement is similar to Remsen and Bernthsen with a few changes which detract somewhat from their systematic and logical arrangement. It is on the whole so much condensed that, well-written as it is, the student must often find difficulty in following the thread connecting the various classes of compounds. The greater part of the book is devoted to the Aliphatic Series more especially to the carbohydrates. This group is neatly compiled but more appropriate for an elementary text of Applied Chemistry. Many of the every-day compounds are barely mentioned and some have been omitted entirely.

The Aromatic Series is too condensed to be of any scientific value to the student. About fifty pages are given to the derivatives of benzene proper, to naphthalene, anthracene, the terpenes, the alkaloids, the glucosides, the proteids and others. There are a good many simple facts stated, and it would seem that the book was perhaps written with the sole object of furnishing the student with these general facts.

It is, however, no longer enough that a text-book of either organic or even inorganic chemistry, be a simple mass of facts and experiments. The subject must be logically presented, leading up to, and proving new facts, by facts already known. At the same time, there must be enough assumed to develop the reasoning powers of the student and to make him feel that he is really doing the work himself. Remsen has struck the key-

note, in this respect in his "Introduction to the Study of the Compounds of Carbon" and it seems to me that it would be exceedingly difficult to place a better elementary text in the hands of the student. In fact, we are not in need of elementary text-books in organic as in inorganic chemistry. The student of organic chemistry begins with a fair knowledge of general and theoretical chemistry and a text like Bernthsen, Krafft or Richter properly used and supplemented by lectures would be far better than a small elementary book. What the organic student is most in need of is a good laboratory book, something the nature of Levy or Fischer. It is to be sincerely hoped now since organic chemistry is gaining ground in our Universities that it may not suffer from scores of poor text-books as inorganic chemistry has done.

UNIVERSITY OF MINNESOTA.

G. B. FRANKFORTER.

A DETAILED COURSE OF QUALITATIVE ANALYSIS. BY ARTHUR A. NOYES
pp. 80. Boston: A. D. MacLachlan, Agent, 214 Clarendon St. 1894.
Price \$1.

This small book of eighty pages aims to present a complete course in inorganic qualitative analysis, so arranged as to be easily followed by the student. The author follows Fresenius, in the main, as to the methods, but has modified them in some particulars. The book is divided into two parts; *viz.*, a clear, concise description of the procedure of the analysis, followed by a series of notes of explanation upon the process.

The main feature of the book, is these explanatory notes. In these the author has sought to instruct the student in all the precautions to be taken to insure accuracy, the possible sources of error, the defects in the processes, the conditions requiring a variation of the procedure, etc.

In one case thirteen, and in others nearly as many, separate notes of this kind are given. It takes, for example, fourteen pages of the book to explain how to deal with the elements of the iron group. While these notes are an excellent feature for students who have become familiar with the usual procedure, it is to be feared that the complexity of conditions they discuss, may confuse the beginner. The description of the procedure is, in most cases, incomplete without the notes, as the appearances

to be expected from the substance tested for are not given. One is obliged to hunt among the notes for the color or appearance of precipitates, etc.

But one test for each metal is given, as a rule, and nowhere are confirmatory tests given. The author plunges the student at once into the separations of the groups, omitting the usual preliminary tests for individual metals, except as they come in the separation. While there is some truth in his statement, that too much of this work is a waste of time, several confirmatory tests for each substance should be found in a complete course in qualitative analysis. Only the more difficult reactions are written out for the student.

There is neither index nor table of contents, which seriously impairs its usefulness for ready reference. While we have pointed out what seem to us its defects, especially for beginners, we must regard its main features as excellent, because of the full explanatory notes. Its chief claim to novelty is in this one feature.

E. H. BARTLEY.

THE JOURNAL

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THE ACCURACY OF THE COMMERCIAL ASSAY FOR SILVER.¹

BY FREDERIC P. DEWEY.

It is generally considered that the fire assay for silver is remarkably accurate when properly carried out. Ricketts says, page 79, "The assay for gold and silver, if conducted carefully, is one of great accuracy. Duplicates of silver should agree to within one-half ounce Troy per ton" (xxx).

In general, and particularly when only small amounts of silver are present, the prevalent idea is correct, but, as shown by the above extract from Ricketts, in considering the accuracy of silver assays, too much stress is laid upon the agreement between duplicates, and I hope to show that, while the actual accuracy of the ordinary fire assay is, in many cases, very great, yet for commercial purposes still greater accuracy is required.

The main conditions which lead to accuracy are the possibility of using large quantities of material and the accuracy attainable in weighing the button, and these apply more particularly when only small amounts of silver are present. When, however, large quantities of silver are present we cannot carry on the process so successfully with so large a quantity of material, and, if we could, we might get a button too large to weigh on a button balance, and thus sacrifice some delicacy of weighing.

It has long been known that there are three sources of loss in assaying; first, from silver going into the slag; second, by silver absorbed by the cupel; third, from volatilization of silver. In dealing with rich materials corrections have been applied, and in the case of bullion it has been sought to correct for all losses by

¹ Read before the Washington Section, April 12, 1894.

running a check assay as near as possible like the test. When, however, we come to consider large quantities of ore, even though they carry only a moderate number of ounces of silver per ton, it is found that greater accuracy of assay for silver is necessary even for this class of material.

This is most clearly shown by a "clean-up" run by the Russell process for lixiviating silver ores. Fifty tons of ore, carrying by the ordinary assay 2,178 ounces of silver, or 43.43 ounces per ton, were treated by the Russell process, and 2,149 ounces of silver recovered, or 99.6 per cent. of the silver shown by the ore. In addition to this the tailings showed 272.25 ounces, or 12.5 per cent. Making a total of 111.5 per cent.

After a thorough investigation of this anomalous result the samples were re-assayed, but the slags and cupels were saved and also assayed, and the results added to the main assay. By this proceeding the ore showed 3.53 ounces more per ton, and the per cent. of silver saved was reduced to 91.5 per cent. Adding to this the 12.5 per cent. remaining in the tailings we have 104 per cent. The increase of silver found in the slag and cupel amounted to 8.1 per cent. of the silver in the ore, and the excess of 4 per cent. on the total may perhaps be assumed as about the volatilization loss in this case.

Attention having been called to the importance of this well-known, but hitherto unappreciated inaccuracy in silver assaying, the Russell Process Company has collected many statistics upon the subject, and I am indebted to a forthcoming pamphlet upon the subject of "plus clean-ups" for much information. I am also indebted to Mr. H. E. Wood, assayer, of Denver, Col., and to the Dewey-Walter Refining Company for many figures used in this paper.

In general, the percentage of the inaccuracy of the ordinary commercial assay varies inversely with the value of the material assayed when figured upon that value.

In order to see this most clearly it is necessary to compare results on the same class of material, and, preferably, made by the same assayer under practically constant conditions. Sometimes when a series of individual results differs irregularly, if the results are grouped considerable regularity may appear. For

instance, on looking at a series of miscellaneous results on ores running from fifteen to forty ounces per ton no regularity may appear, but if the results are grouped in periods differing by five ounces per ton they may become very regular in the variation. While different assayers working on the same material may show some regularity, they may also vary greatly.

For instance, a group of results on tailings arranged according to the increase in value by commercial assay shows as follows:

| Material. | Grade.
Ounces per
ton. | Value
commercial
assay.
Ounces per
ton. | Value in
slag and
cupel.
Ounces per
ton. | Corrected
value.
Ounces per
ton. | Percentage in
slag and
cupel. |
|---------------|------------------------------|---|--|---|-------------------------------------|
| Tailings..... | 1- 3 | 1.8 | 0.5 | 2.3 | 21.8 |
| " | " | 2.8 | 0.4 | 3.2 | 12.5 |
| " | 3- 5 | 3.0 | 0.6 | 3.6 | 16.7 |
| " | " | 3.9 | 1.0 | 4.9 | 20.0 |
| " | " | 4.0 | 0.5 | 4.5 | 11.4 |
| " | 5- 7 | 5.5 | 0.6 | 6.1 | 10.0 |
| " | " | 6.0 | 1.3 | 7.3 | 17.8 |
| " | " | 6.2 | 1.2 | 7.4 | 16.1 |
| " | 7- 9 | 7.5 | 1.4 | 8.9 | 15.7 |
| " | " | 8.3 | 0.9 | 9.2 | 10.1 |
| " | 9-11 | 9.6 | 1.6 | 11.2 | 14.3 |
| " | " | 9.7 | 1.6 | 11.3 | 14.2 |
| " | " | 9.8 | 1.3 | 11.1 | 10.0 |
| " | 11-13 | 12.2 | 1.8 | 14.0 | 13.0 |
| " | 15-20 | 17.5 | 1.6 | 19.0 | 16.9 |
| " | " | 18.5 | 1.8 | 20.3 | 8.9 |

When, however, we take out of this table the results by a single assayer, we have:

| Material. | Grade.
Ounces per
ton. | Value
commercial
assay.
Ounces per
ton. | Value in
slag and
cupel.
Ounces per
ton. | Corrected
value.
Ounces per
ton. | Percentage in
slag and
cupel. |
|---------------|------------------------------|---|--|---|-------------------------------------|
| Tailings..... | 1- 3 | 1.8 | 0.5 | 2.3 | 21.8 |
| " | 3- 5 | 3.9 | 1.0 | 4.9 | 20. |
| " | 5- 7 | 6.0 | 1.3 | 7.3 | 17.8 |
| " | 7- 9 | 7.5 | 1.4 | 8.9 | 15.7 |
| " | 9-11 | 9.6 | 1.6 | 11.2 | 14.3 |
| " | 11-13 | 12.2 | 1.8 | 14.0 | 13. |
| " | 13-20 | 18.5 | 1.8 | 20.3 | 8.9 |

When we group results by five ounce periods we have:

| Material. | Grade.
Ounces per
ton. | Value
commercial
assay.
Ounces per
ton. | Value in
slag and
cupel.
Ounces per
ton. | Corrected
value.
Ounces per
ton. | Percentage in
slag and
cupel. |
|---------------|------------------------------|---|--|---|-------------------------------------|
| Tailings..... | 1- 5 | 2.8 | 0.7 | 3.5 | 18. |
| " | 5-10 | 7.8 | 1.4 | 9.2 | 15.2 |
| " | 10-15 | 12.2 | 1.8 | 14.0 | 13. |
| " | 15-20 | 18.0 | 1.7 | 19.7 | 8.6 |

It has been found that the character of the ore influences the results. In three kinds of ores, base, containing seventy-five per cent. sulphurets, partially oxidized, and completely oxidized, carrying from 16.5 to 34.6 ounces of silver per ton, the percentages of silver found in the slag and cupel were as follows:

| Base. | Intermediate. | Oxidized. |
|-------|---------------|-----------|
| 5.7 | 8.2 | 9.8 |
| 6.8 | 7.8 | 11.3 |

the results on the top line being obtained by scorification and those on the bottom line by crucible assay, of the same ore in each case.

It follows then, that when ores consisting of mixtures of altered and unaltered material are considered, the proportion between these two should be known and allowed for when comparing results on similar grades of ore, if one would discover the regularity in the variation of the results.

Again, whether the ore is raw or roasted, or has been washed, influences the result, roasted ore being generally more inaccurate than raw.

A heterogeneous table of results on ores running from ten to fifty ounces per ton is as follows:

| Material. | Grade.
Ounces per
ton. | Value
commercial
assay.
Ounces per
ton. | Value in
slag and
cupel.
Ounces per
ton. | Corrected
value.
Ounces per
ton. | Percentage in
slag and
cupel. |
|-----------|------------------------------|---|--|---|-------------------------------------|
| Ore | 10-15 | 12.5 | 1.3 | 13.8 | 6.4 |
| " | 15-20 | 17.6 | 1.8 | 19.4 | 9.0 |
| " | 20-25 | 22.4 | 1.9 | 24.3 | 7.8 |
| " | " | 23.1 | 2.0 | 25.1 | 8.0 |
| " | " | 23.8 | 4.8 | 28.6 | 13.0 |
| " | " | 23.9 | 4.5 | 28.4 | 15.8 |
| " | " | 24.1 | 5.9 | 29.7 | 18.8 |
| " | " | 24.3 | 3.3 | 27.6 | 12.0 |
| " | 25-30 | 26.6 | 2.5 | 29.1 | 8.6 |
| " | " | 27. | 4.0 | 31.0 | 13.0 |

| Material | Grade.
Ounces per
ton. | Value
commercial
assay.
Ounces per
ton. | Value in
slag and
cupel.
Ounces per
ton. | Corrected
value.
Ounces per
ton. | Percentage in
slag and
cupel. |
|-----------|------------------------------|---|--|---|-------------------------------------|
| Ore | 25-30 | 27.2 | 2.9 | 30.1 | 9.7 |
| " | " | 28. | 4.6 | 32.6 | 14.1 |
| " | " | 28.4 | 3. | 31.4 | 9.0 |
| " | " | 28.9 | 1.6 | 30.5 | 5.0 |
| " | " | 29.7 | 2.8 | 32.5 | 8.6 |
| " | 30-35 | 30.4 | 3.6 | 34.0 | 10.6 |
| " | " | 30.6 | 2.0 | 32.6 | 6.1 |
| " | " | 30.7 | 3.9 | 34.6 | 11.3 |
| " | " | 31.6 | 3.4 | 35.0 | 10.0 |
| " | " | 31.8 | 2.3 | 34.1 | 7.0 |
| " | " | 31.9 | 3.9 | 35.8 | 10.9 |
| " | " | 32.3 | 3.7 | 36.0 | 10.0 |
| " | " | 33. | 4.1 | 37.1 | 10.8 |
| " | " | 33.1 | 2.8 | 35.9 | 7.8 |
| " | " | 33.6 | 3.2 | 36.8 | 8.7 |
| " | 35-40 | 36.7 | 3.1 | 39.8 | 7.8 |
| " | " | 36.9 | 3.3 | 40.2 | 8.2 |
| " | " | 37.4 | 4.3 | 41.7 | 10.0 |
| " | " | 37.65 | 2.25 | 39.9 | 5.6 |
| " | " | 38.2 | 2.8 | 41.0 | 6.8 |
| " | 40-45 | 42.1 | 3. | 45.1 | 6.7 |
| " | " | 42.3 | 2.3 | 44.6 | 5.2 |
| " | " | 42.4 | 2.4 | 44.8 | 5.4 |
| " | " | 44.7 | 4.3 | 49. | 8.8 |
| " | 45-50 | 45.5 | 2.4 | 47.9 | 5.0 |

The variation shown by the above table is very diverse, but the following grouping by five ounce periods, and according to the character of the ore, shows the inverse variation beautifully :

| Material. | Grade.
Ounces per
ton. | Value
commercial
assay.
Ounces per
ton. | Value in
slag and
cupel.
Ounces per
ton. | Corrected
value.
Ounces per
ton. | Percentage in
slag and
cupel. |
|----------------|------------------------------|---|--|---|-------------------------------------|
| Roasted ore .. | 20-25 | 23.5 | 3.2 | 26.7 | 12. |
| " " .. | 25-30 | 27.3 | 3.5 | 30.8 | 11.4 |
| " " .. | 30-35 | 31.6 | 2.8 | 34.4 | 8.1 |
| " " .. | 35-40 | 36.8 | 3.2 | 40.0 | 8. |
| " " .. | 40-45 | 42.3 | 2.7 | 45.0 | 6. |
| Raw ore | 20-25 | 24.2 | 4.6 | 28.8 | 16. |
| " " | 25-30 | 27.7 | 3.5 | 31.2 | 11.2 |
| " " | 30-35 | 31.8 | 3.8 | 35.6 | 10.7 |
| " " | 35-40 | 37.5 | 3.3 | 40.8 | 8.1 |
| " " | 40-45 | 43.5 | 3.3 | 46.8 | 7.1 |
| " " | 45-50 | 45.5 | 2.4 | 47.9 | 5. |

While the amount of silver recovered from the slag and cupel in the case of ordinary ores is small, when stated per ton of ore, yet when a year's operations, involving ten, twenty, thirty, or more thousands of tons, are considered the difference between an ordinary and a corrected assay amounts to quite a respectable sum, and becomes well worthy of consideration in these times of low prices for silver.

When we consider rich materials, such as high-grade ore and the products of the Russell process, for instance, the slag and cupel loss on a single ton becomes considerable, and with very rich products, such as lixiviation sulphides, particularly when they carry a large percentage of copper, as in the regular Russell sulphides, this loss may amount to several hundred ounces per ton. It has been customary to use the slag and cupel assay on rich products and it was employed on the "clean-up" referred to.

I am indebted to Mr. H. E. Wood, assayer, No. 1,744 Arapahoe St., Denver, Col., for a series of results on sulphides, varying from poor to rich.

The following details give the results on assaying sulphides—scorification method. 1-20 A. T. of sulphides used, and scorification slag and cupel from original assay then rescorified and cupelled with result shown. Classified according to the grade the losses were as follows:

| | | | |
|---------------|------------|--------------|-----------------|
| Under 500 | Average of | 1 Lot..... | 4.170 per cent. |
| 500 to 1,000 | " " | 6 Lots | 2.910 " " |
| 1,000 " 1,500 | " " | 14 " | 2.996 " " |
| 1,500 " 2,000 | " " | 9 " | 2.540 " " |
| 2,000 " 2,500 | " " | 12 " | 2.109 " " |
| 2,500 " 3,000 | " " | 21 " | 1.867 " " |
| 3,000 " 3,500 | " " | 19 " | 1.860 " " |
| 3,500 " 4,000 | " " | 19 " | 1.821 " " |
| 4,000 " 4,500 | " " | 10 " | 1.695 " " |
| 4,500 " 5,000 | " " | 7 " | 1.700 " " |
| 5,000 " 5,500 | " " | 4 " | 1.845 " " |
| 5,500 " 6,000 | " " | 4 " | 1.895 " " |
| 6,000 " 6,500 | " " | 1 Lot | 1.630 " " |
| 6,500 " 7,000 | " " | 4 Lots | 1.777 " " |
| 7,000 " 7,500 | " " | 2 " | 1.640 " " |
| 7,500 " 8,000 | " " | 1 Lot | 1.420 " " |
| 8,000 " 8,500 | " " | 3 Lots | 1.537 " " |
| 9,000 " 9,500 | " " | 3 " | 1.460 " " |

| | | | |
|------------------|------------------|-------|-----------------|
| 10,500 to 11,000 | Average of 1 Lot | | 1.570 per cent. |
| 11,500 " 12,000 | " " 1 " | | 1.340 " " |
| 12,000 " 12,500 | " " 1 " | | 1.270 " " |
| 17,000 " 17,500 | " " 1 " | | 1.260 " " |

The average slag and cupel absorption on the 144 lots was 2.03 per cent. of the total contents.

The following table shows the results obtained on eleven lots of regular Russell sulphides when assayed by the following method:

"Weigh out one-twentieth ($\frac{1}{20}$) of an assay ton of sulphides, fifty-five grams of granulated test-lead, and two (2) to three (3) grams of fused borax. One-half of the lead is put in the bottom of the scorifier and hollowed out; the sulphides are put into the hollow and the rest of the lead poured over them; the borax is then placed on top. The assay is then conducted in the usual way. The slag and cupel shall be ground up and assayed, and the result added to the main assay."

This method is the result of a great deal of work and has been adopted as most suitable for this class of material.

In the table are given, first, the results of plain scorification assay; second, the ounces per ton found in the slag and cupel; third, the percentage in slag and cupel; fourth, the total silver found by adding the slag and cupel silver to the scorification silver by one assayer; fifth, the total silver as found by another assayer upon the same samples, and finally, the difference between the two assayers.

| Ounces per ton by commercial assay. | Ounces per ton in slag and cupel. | Per cent. in slag and cupel. | Total ounces per ton. | | Differences. | |
|-------------------------------------|-----------------------------------|------------------------------|-----------------------|--------------|--------------|--------|
| 1st assayer. | 1st assayer. | 1st assayer. | 1st assayer. | 2nd assayer. | Plus. | Minus. |
| 8,675.20 | 144.11 | 1.622 | 8,819.31 | 8,782 | 37.31 | |
| 10,074.25 | 189.35 | 1.844 | 10,263.60 | 10,119 | 144.60 | |
| 10,783.35 | 189. | 1.720 | 10,972.35 | 10,938 | 34.35 | |
| 10,902.30 | 194.38 | 1.752 | 11,096.68 | 11,220 | | 123.32 |
| 11,015.73 | 191.69 | 1.710 | 11,207.42 | 11,090 | 117.42 | |
| 11,238.40 | 175.22 | 1.535 | 11,413.62 | 11,548 | | 134.38 |
| 11,828.75 | 176.72 | 1.471 | 12,005.47 | 12,046 | | 40.53 |
| 12,566.55 | 199.21 | 1.560 | 12,765.76 | 12,821 | | 55.24 |
| 12,665.85 | 199.87 | 1.553 | 12,865.72 | 12,841 | 24.72 | |
| 13,001.65 | 229.84 | 1.737 | 13,231.49 | 13,187 | 44.49 | |
| 13,625.50 | 226.52 | 1.635 | 13,852.02 | 13,919 | | 66.98 |

On comparing results on individual lots considerable variation will be found between the two assayers, but on considering the total amount of silver involved the difference becomes quite small. By the first assayer these eleven lots contain 236,418.99 ounces of silver, while by the second they contain 236,483.88 ounces, the difference between the two being only 54.89 ounces. This amount is 0.0232 per cent. of the smallest total of ounces found, and 0.0095 per cent. of the weight of sulphides involved. This shows that when carefully and properly executed the method gives concordant results on averaging a sufficient number of assays.

As showing the difference which may occur by this method of assaying, besides noting the individual difference above, between the two assayers, it may be added that one of these found the following difference on assaying the same sample at different times:

| | |
|------------|---------------------|
| No. 1..... | 144 ounces per ton. |
| " 2..... | 90 " " " |
| " 3..... | 112 " " " |

Making a difference of 527.36 in the total silver involved.

Also on a lot of sulphides containing 218,324 ounces¹ by one assayer, a second assayer obtained 0.587 per cent. less on the same samples, and in a second comparison between the first assayer and the same smelting works, representing 156,091, the difference was 1.355 per cent.

The following results were obtained in my laboratory by Mr. Charles Earl:

| Total silver.
Ounces per ton. | Silver in slag and
cupel.
Ounces per ton. | Percentage in slag
and cupel. |
|----------------------------------|---|----------------------------------|
| 9,156.3 | 244. | 2.664 |
| 9,590. | 257.5 | 2.685 |
| 9,828.2 | 250. | 2.543 |
| 10,077.95 | 198.25 | 1.967 |
| 10,456. | 266. | 2.544 |
| 10,759. | 244.5 | 2.272 |
| 10,861.5 | 282.5 | 2.6 |
| 11,700.2 | 198.66 | 1.697 |
| 12,087.8 | 233.3 | 1.93 |
| 13,804.5 | 250.33 | 1.813 |

¹ *Trans. A. I. M. E.*, Pamphlet Edition. Product and Economical Results of the Marsac Refinery for the year 1892, by C. A. Stetefeldt, p. 9.

In using this method Mr. Earl usually starts four assays of each sample. As he has found the charge rather destructive to scorifiers it is not unusual to lose an assay. In two sets of four results the differences between the highest and lowest individual results were 49.6 and 95 ounces per ton. In five sets of three results the differences were 36, 54, 94, 98, and 152.2 ounces per ton. As each one of a set of assays was carried through under practically the same conditions as the others these differences may seem rather high, but the total ounces represented by these seven assays by Mr. Earl was 121,346.53 ounces, while another very expert assayer by this method, working upon the same samples, found 121,446.56 ounces, showing a difference of only 99.93 ounces on the total number of ounces involved. The following table shows the individual variations:

| Total ounces per ton. | | Differences. | |
|-----------------------|--------------|--------------|--------|
| | | Plus. | Minus. |
| 6,769 | 6,847 | .. | 78 |
| 9,400.3 | 9,430 | .. | 29.7 |
| 9,590 | 9,524 | 66 | ... |
| 9,928 | 9,880 | 48 | ... |
| 10,078 | 10,119 | .. | 41 |
| 10,456 | 10,446 | 10 | ... |
| 10,759 | 10,833 | .. | 74 |

The following tables summarize a large quantity of determinations and are taken from the pamphlet by the Russell Process Company referred to:

| Material. | Grade.
Ounces
per ton. | Value
commercial
assay.
Ounces
per ton. | Value in
slag and
cupel.
Ounces
per ton. | Corrected
value.
Ounces
per ton. | Percentage
slag and
cupel. |
|-------------------|------------------------------|---|--|---|----------------------------------|
| Lead carbonate... | 1- 50 | 5.2 | 0.8 | 6.0 | 15.4 |
| " " ... | 50- 100 | 64.8 | 3.2 | 68 | 5.1 |
| " " ... | 100- 500 | 447.6 | 12.4 | 460 | 2.6 |
| Base sulphides... | 100- 500 | 394 | 37 | 431 | 8.6 |
| " " ... | 500- 1,000 | 766 | 41 | 807 | 5.1 |
| " " ... | 1,000- 1,500 | 1,227 | 36 | 1,263 | 2.9 |
| " " ... | 2,000- 3,000 | 2,527 | 88 | 2,615 | 3.2 |
| " " ... | 3,000- 4,000 | 3,289 | 113 | 3,402 | 3.2 |
| " " ... | 4,000- 5,000 | 4,962 | 116 | 5,078 | 2.2 |
| Regular sulphides | 100- 1,000 | 493 | 45 | 5,538 | 8.4 |
| " " ... | 1,000- 2,000 | 1,624 | 83 | 1,707 | 4.9 |
| " " ... | 2,000- 4,000 | 2,807 | 60 | 2,867 | 2.1 |
| " " ... | 4,000- 6,000 | 5,291 | 98 | 5,389 | 1.8 |

| Material. | Grade.
Ounces
per ton. | Value
commercial
assay.
Ounces
per ton. | Value in
slag and
cupel.
Ounces
per ton. | Corrected
value.
Ounces
per ton. | Percentage
slag and
cupel. |
|--------------------|------------------------------|---|--|---|----------------------------------|
| Regular sulphides | 6,000- 8,000 | 7,362 | 110 | 7,472 | 1.5 |
| " " | 8,000-10,000 | 8,604 | 128 | 8,732 | 1.5 |
| " " | 10,000-12,000 | 10,538 | 150 | 10,698 | 1.5 |
| " " | 12,000-14,000 | 12,842 | 218 | 13,060 | 1.7 |
| " " | 14,000-16,000 | 14,866 | 180 | 15,046 | 1.2 |
| Refinery residues, | 14,000-16,000 | 15,952 | 159 | 16,111 | 1. |
| | Fine. | Fine. | Fine. | Fine. | |
| Base bullion | 300- 500 | 400 | 8 | 408 | 2. |
| Fine " | 998- 1,000 | 987 | 11.5 | 998.5 | 1.2 |

| Material assayed. | Grade of
value. | Range of
inaccuracy. | Average
inaccuracy. |
|---|--------------------|-------------------------|------------------------|
| Tailings | 1- 20 | 18 - 8.6 | 13.7 |
| Washed ore..... | 15- 35 | 13 -10.0 | 10.4 |
| Raw ore..... | 20- 50 | 16 - 5.0 | 9.7 |
| Roasted ore | 20- 45 | 12 - 6.0 | 9.1 |
| Lead carbonate | 50- 100 | 5.1- 2.6 | 3.8 |
| Base sulphides | 1,000- 5,500 | 5.0- 1.8 | 3.0 |
| Regular sulphides..... | 2,000-16,000 | 2.8- 1.2 | 1.7 |
| Copper-silver bullion, 300 "fine" | | 2.0 | 2.0 |
| Fine bullion, 999.3 "fine" | | 1.1 | 1.1 |

In a number of cases the slag and cupel have been assayed separately, but there does not seem to be any uniformity of results, except that the cupel silver is generally much greater than the slag silver, although in one case they were both the same, 0.8 ounce. In a set of twenty-nine assays, running from tailings at 6.2 ounces per ton to ore at 44.7, the cupel silver varied from 0.8 to 5.4 ounces per ton, and the slag silver from 0.1 to 1.8 ounces per ton; the lowest cupel silver was on 18 ounce ore and the highest on 24.1 ounce ore; the lowest slag silver was on 26 ounce ore, and the highest on 32.4 ounce ore, and both these assays were made by the crucible method. In only two cases was the cupel silver less than 1 ounce per ton, and one of these was on the 6.2 ounce per ton tailings, and in only two cases was the slag silver over 1 ounce per ton.

In the case of the nearly proof silver produced at the Marsac refinery, by the writers process, the straight assay shows 987 fine, corrected for slag and cupel absorption it becomes 998.5 fine, as given in the table, while with a check assay to correct the volatilization loss it becomes 999.3 fine.

When we come to consider the percentage of inaccuracy when figured upon the total material assayed we find that it is somewhat irregular but generally it follows the silver contents of the material, and in the case of rich products, becomes very large. Thus, in 2.3 ounce tailings the silver equals 0.0079 per cent. of the total and a 21.8 per cent. loss on this equals only 0.0017 per cent. of the total. On the other hand, in a 17,500 ounce sulphide the silver equals 60 per cent. of the total, but the comparatively small loss of 1.26 on this equals 0.756 per cent. of the total.

The following table gives a few results upon this point:

| Material. | Grade.
Ounces. | Silver
per cent. of total. | Inaccuracy
of silver. | per cent.
of total. |
|--------------------|-------------------|-------------------------------|--------------------------|------------------------|
| Tailings..... | 2.3 | 0.0079 | 21.8 | 0.0017 |
| Ore | 20.3 | 0.0696 | 8.9 | 0.0062 |
| " | 30.5 | 0.1011 | 5. | 0.0051 |
| " | 31 | 0.1063 | 13. | 0.0138 |
| " | 49 | 0.1680 | 8.8 | 0.0148 |
| Base sulphides ... | 431 | 1.477 | 8.6 | 0.12602 |
| " " ... | 5,078 | 17.41 | 2.2 | 0.38302 |
| Regular sulphides | 5,538 | 18.98 | 8.4 | 1.59432 |
| " " | 10,698 | 36.33 | 1.5 | 0.54495 |
| " " | 15,046 | 51.58 | 1.2 | 0.61896 |
| " " | 17,500 | 60.00 | 1.26 | 0.756 |

The question is sometimes asked if some wet method would not be better than fire assaying, but at present no such method is available.

While the correction for slag and cupel loss is easily made, and ought always to be made when accurate statistics are kept, there is yet the volatilization loss to correct, and some means of doing this is very desirable. While a check assay answers very well for bullion it would hardly be possible to construct check material for the varying characters of ores and products ordinarily met with. •

As chemists we should all be interested in attaining the highest accuracy possible in our analytical work, but in this case, aside from the question of accuracy, and also the money value of the silver involved, when many thousand tons of ore are considered, this point has a very important practical application in indicating and bringing out unsuspected losses in mill opera-

tions. For instance, in one case, by ordinary assays of the ore, the mill showed to be extracting 87 per cent. of the silver in the ore, which was considered good work. Corrected assays of the ore showed, however, that the extraction was only 79.3 per cent. This led to an investigation, which showed that there was a volatilization loss of 10.9 per cent. in roasting the ore. This has been cut down to 5 per cent., with the expectation of reducing it still more.

In another case the extraction plus the tailings silver was 102.7 per cent., but corrected assays showed it to be only 87.1 per cent. This was brought up to 97 per cent.

These figures show that the commercial assays of ores are too unreliable if accurate mill statistics are desired.

THE ACHIEVEMENTS AND AIMS OF PHYSICAL CHEMISTRY.¹

By J. E. TREVOR.

Received June 7, 1894.

CHEMICAL changes, in common with all other natural processes, are in their ultimate nature transformations of energy. The study of chemical processes is therefore a study of the energy phenomena which they involve. Chemical reactions may absorb or take up heat, changes of density may occur whereby work is done, electrical energy and radiant energy may be produced. But the mutual relations of heat, work, electricity, and the like, involving the characteristic factors, temperature, pressure, tension, force, potential, etc., form the subject-matter of the science of Physics, and hence it is that the study of chemical processes as such has come to be known as the *Physical Chemistry*. The object of this branch of science is to discover the simple relations connecting the various types of chemical phenomena, and to make of these relations a coherent whole.

The Physical Chemistry is a new science. Up to eight years ago nothing serious had been attempted in the way of generalization. Very important discoveries had been made before that time it is true, yet they were of a wholly disconnected character and their bearing upon a general theory of chemical processes

¹ Read before the Midwinter Fair Congress of Chemists at San Francisco, June 7, 1894.

was not seen. Prominent among these achievements of a generation whose efforts have now become history stand the experimental work of Thomsen and Berthelot in thermo-chemistry, the investigations of Kopp in stoichiometry, the dissociation theory of Horstmann and of Gibbs, the brilliant researches of Helmholtz in electro-chemistry, and that flash of insight which led to the discovery of the law of mass action. Nor is the present generation proving itself unworthy of this inheritance of scientific achievement; the chemical equilibrium, the electro-chemistry, and the thermodynamical generalizations of to-day are supplying a fit sequel to this story of the past.

In 1886 appeared van't Hoff's first paper upon the theory of solutions. It was immediately followed by that extended series of monographs, written by such men as Ostwald, Nernst, Arrhenius, Planck, Riecke, and many others, which has made the thermodynamical theory of solutions one of the most remarkable conquests of the science of chemistry. Van't Hoff's discovery that the inner energy of a dissolved substance when dilute is independent of the volume of its solution led at once to the discovery of simple relations between the physical properties of solutions and their molecular concentrations, *i. e.*, to a series of novel methods for the determination of molecular weights; it brought about an unforeseen extension of the law of mass action to the solution-equilibria of both homogeneous and heterogeneous systems; it led to a strict formulation of the influence of temperature upon chemical equilibrium and the velocities of reactions, to a mathematical theory of hydrodiffusion, to a comprehensive theory of concentration currents and of the voltaic cell, and to an unexpected culmination of Ostwald's exhaustive investigations upon the chemical affinities of aqueous acids and bases. This breathless succession of advances constitutes one of the most interesting and exciting chapters of the history of chemical theory.

It is being succeeded at the present time by work of a more general and wide-reaching character. The great generalizations of thermodynamics are hastening the day when chemistry shall become a deductive science. Planck, of Berlin, has recently directed especial attention to the following course of reasoning.

There are certain processes, such as the conduction of heat from a hot to a cold body, or the diffusion of a dissolved substance from a high concentration to a lower one, which are irreversible—they take place only in one direction. This fact may be shown to require the conclusion that the general trend of natural processes is in an assignable direction; the general state of things tends all one way. If this were not so it would be possible to reverse history, to make trees grow down into seeds, and to awaken fossils to quivering, pulsating life.

The strict formulation which represents this general tendency furnishes, therefore, a means of determining definitely the direction which any given natural process, chemical or otherwise, must pursue; and it leads in consequence to an exact relation between the energy factors upon which the final state of the material system concerned is made to depend, a relation which combines in one expression every law of chemical equilibrium. From it can be derived in order all the laws of isothermal chemical equilibrium in homogeneous and in heterogeneous systems, and those which represent the effect of changes of temperature and of pressure in displacing such equilibria; it yields further the laws relating to the many physico-chemical properties of solutions which depend upon the vapor pressures; and it furnishes, finally, the almost numberless theorems of electro-chemistry. Thus it is seen that from the assumption of a simple fact of experience, the irreversibility of heat conduction, a mathematical theory of chemical changes is obtained which organizes into a coherent and logically connected whole all the exact relations of chemical science. The deductive value of this theory is enormous, in that it clearly points out the limits of our knowledge in every direction. And for the reason that the system is uniform and falls into a logical order it becomes of the greatest service in aiding the conception of chemical theory as a whole and in fixing in the mind the relations between its parts.

Another form of the same fundamental idea has been employed by the eminent French mathematical physicist, Duhem, in developing a systematic treatment of the theory of chemistry. From the properties of his *thermodynamical potential* (taken from the thermodynamical studies of Willard Gibbs) he has evolved

an orderly discussion of the theory of dissociation, the continuity of the liquid and gaseous states, and the general theory of the chemical and physical equilibria of fluid mixtures, all of which is characterized throughout by strict uniformity of method and an unusual elegance of mathematical style.

These two methods of research are essentially identical, for they are based upon the same principle, and they both refer the solution of every problem to the properties of a single function of quantities which fix the state of the system concerned. In this respect they mark a distinct advance in the study of the science of chemistry.

The eminent fruitfulness of these thermodynamical methods has led to a fuller appreciation of the bearing and significance of the great energy generalization which they involve, and upon which, indeed, the entire framework of modern physical science really rests. If chemistry be in its ultimate nature, an energy science, chemists obviously must study those energy transformations which constitute its phenomena. In a chemical change different energies come into play, and the change continues until they hold one another exactly in balance. This balance determines, therefore, what the final state of the system in question shall be. Two energy forms are in equilibrium when a possible variation of one is exactly compensated by the corresponding variation of the other. All that is necessary then to determine the final state which any given material system must assume is to represent mathematically the possible variations of its opposed energies and to set these variations equal. This procedure is identical with that which is employed in Statics to investigate the equilibria of mechanical systems. When applied systematically to the different types of chemical action it yields a rational classification of chemical processes, and, in a logical sequence, all of the known elements of the modern physical chemistry. This reconstruction of theoretical chemistry upon the basis of the Energy Theory is one of the most brilliant of Ostwald's many splendid contributions to science.

It is important to observe that the great advances of recent years in the theory of chemical action have not been made with the aid of the kinetic-molecular hypothesis. The assumption of

atoms and molecules has been a constant hindrance to the progress of rational chemical theory. The "Kinetic Theory of Gases" has been able to account for the behavior of gases only in an imperfect manner, and it has not been able to account at all for the laws of chemical equilibrium and the properties of solutions. The fact that gases react in simple volume relations justifies the selection of a definite volume as the chemical unit, the relative weight of this volume becoming then the so-called molecular weight, but it justifies in no wise the conclusion that gases are composed of discrete particles. This unwarranted assumption was made because of a desire to "explain" from the behavior of a purely mechanical system the observed characteristics of gases. Yet the behavior of the model is, after all, only approximately that of the gas. And, moreover, it is not the province of science to "explain" anything, certainly not to explain phenomena by reference to unrealizable mechanical constructions. It is becoming more and more clearly seen, day by day, that the business of science is to *describe* phenomena in a simple manner, to seek actual relations between measurable quantities, to deal only with things which can be handled and observed. Hypotheses must be employed, if at all, only provisionally and as analogies.

There is no desire to deny that the molecular hypothesis has been fruitful of results; any hypothesis may lead to work whereby knowledge is gained. Yet this one has nearly outlived its usefulness, and it will be employed less and less in the future by those chemists who refuse to believe upon insufficient evidence. As an accepted hypothesis its days are numbered. In the place of the Molecule appears the Molecular Weight, a sharply defined quantity whose conception does not transcend experience.

The average student of chemistry is trained to confuse the real with the hypothetical. He believes molecular formulas and molecules to involve each other, whereas, the former represent facts while the latter are creations of fancy. The molecular formulas of our chemical equations possess a very real and important signification, and this is no less true of the structural formulas which form at the present time so important a feature of the technical apparatus of organic chemistry. These structural formulas

are valuable mnemonic expressions for the individual chemical character of the substances in question, and when employed for what they represent their value is not to be underestimated. Yet one must not for a moment suppose that they supply a picture of the mechanical structure of small particles of the substances; this idea is a purely hypothetical one, and at the best represents nothing more than the original facts. The symbols, properly used, represent the facts and not the hypothesis.

The general methods which give to the best modern thought its distinctive character appeal to experience alone. Things other than observable fact do not fall within their province, such things are not objects of human knowledge. It should not need emphasis that this is the only natural and reasonable basis for a science of the facts of nature. And it cannot be denied that our first real insight into the nature of chemical processes has been gained by the application of these straightforward methods.

The age of mechanical hypotheses is of the past. The desire to replace known laws by unproven or unprovable assumptions is passing away. And it can now be clearly recognized that the view which seeks to place mechanics at the base of all departments of physical science is, in its thoughtless exclusion of energies other than mechanical, a prejudice. Now, the thermodynamical systems and the energy doctrine involve only accessible facts. They are built upon no assumption other than the irreversibility of some spontaneous process, or the observed conservation of the energy of an isolated system. Their aim is to increase knowledge, and not representations of knowledge, to seek out the facts of nature and the wonderful and simple relations subsisting among these facts. And in this there are notable instances of what is fittingly termed *Physical Theory*. The distinction between theory and hypothesis can now be sharply drawn, the Hypothesis is a mechanical construction substituted by the imagination for things as they actually are, the Theory is an organized system of logical consequences drawn from the established facts of experience. Mechanical Hypotheses have dimmed the glory of the history of chemistry, Physical Theory endows chemistry with the attributes of an exact science.

The subject of electro-chemistry has become, in recent years, a

prominent feature of the physical chemistry. The energy liberated in chemical changes may appear as electrical energy; or electrical energy may, during a chemical process, be transformed into the inner energy of the products of the reaction. Our knowledge of these things has had a contentious and a profoundly interesting history. The strugglings and gropings of a hundred years lie between this time and that in which the first observations of electro-chemical action were made by Galvani and Volta. The intervening years have been largely occupied by a study of the phenomena of electrolysis pure and simple. The insight thereby gained into the nature of this process has led to a clear conception of what takes place in the various types of voltaic cell, and has, in consequence, rendered accessible to immediate calculation all the essential details of the transformation between the free energy of the chemical action in a cell and the electrical energy which is produced. This comprehensive theory of electro-chemistry is one of the greatest results which has followed the introduction of the energy theory into chemistry, it is the fitting close of a century of effort.

And now that such a result has been reached it is a matter for congratulation that the event is to be marked by a great literary monument. This is Ostwald's work on electro-chemistry, at the present moment passing through the press, a book which is to give a full and clear account of the entire development of the subject from its beginnings.

The influence which has been exerted upon physical chemistry by its literature is of the most interesting character. Widespread interest in physical chemistry as an independent subject dates, probably, from the publication of Ostwald's *Lehrbuch der allgemeinen Chemie*, in 1887. The interest thus aroused was immediately intensified by the appearance of van't Hoff's thermodynamical theory of dilute solutions, and the remarkable series of theoretical and experimental discoveries which followed in its train. This period marks, undoubtedly, the beginning of physical chemistry as a connected and organized science. Its development since then, due to no small extent to the efforts of Ostwald and van't Hoff and their pupils, has found a fit channel for expression in the pages of the *Journal of Physical Chemistry*

(*Zeitschrift für physikalische Chemie*), whose first number appeared also in 1887. A systematic account of the present status of the science is now being supplied by a new edition of Ostwald's *Lehrbuch*, which has in the meantime grown to be a monumental work in three volumes, two of which are already in print. And it is well to add that the general desire for a text-book of less exhaustive nature has been well met by the briefer "*Outlines*" by the same author, and the "*Theoretical Chemistry*" of Nernst. Due reference has been already made to Ostwald's magnificent publication upon electro-chemistry.

The great demand now to be made upon the future is for a book upon the *General Theory of Energy*; a work in which the relations of natural phenomena to one another may be brought into a clear light, a work in which we may finally see effaced the artificial distinctions between the subjects of Chemistry, Mechanics, Thermodynamics, Electricity, etc., which, as we have them now, are partly historical, partly physiological, partly conventional, and wholly unsatisfactory.

The science of Physical Chemistry is, at the present moment, in a stage of the most active development. Every month brings to the light some startling experimental discovery, or some broader generalization. The general methods now in use have already begun to furnish a complete thermodynamical theory of solutions for all concentrations, a thorough grasp of the conditions of chemical equilibrium in complex heterogeneous systems, a really adequate comprehension of the phenomena of galvanic polarization, and an exact definition of chemical affinity. These are the things of to-day, what the morrow may bring forth is for no man to say. Yet it is certain that the chemistry of the future will deal with fact and not with fancy, and that its immediate aim will be the establishment of exact relations between those quantities upon which the state of every material system ultimately depends. For it is in this way, and in this way only, that a real insight into the nature of chemical processes will finally be attained.

CORNELL UNIVERSITY,
May, 1894.

PROTEIDS OF THE WHEAT KERNEL.¹

BY THOMAS B. OSBORNE AND CLARK L. VOORHEES.

THE importance of wheat as a breadstuff, and the fact that its superiority over all other cereals for bread-making mainly depends on the properties of the proteids composing the gluten which wheat dough yields when cautiously washed with water, justify giving here in some detail an account of the present state of knowledge regarding the proteids of wheat.

The wheat used in our work was of two kinds. One of these, Scotch Fife, a hard spring wheat, raised in Minnesota, was obtained through the kindness of Dr. D. N. Harper, late chemist of the Minnesota Experiment Station. It was carefully selected, free from all other varieties, and was milled under the supervision of Dr. Harper, who supplied us with samples of the various mill products, together with some of the unground wheat. Two grades of flour were used; namely, "patent flour," made from the finest and purest middlings, and "straight flour," from the coarser and less pure middlings. The "shorts," chiefly composed of the outer coating of the seeds together with adhering portions of the endosperm, was also examined. Samples of whole wheat flour were prepared as required from the wheat by grinding small quantities in the laboratory mill. The other wheat used was a variety of winter wheat known as "Fultz." This was procured from Mr. F. S. Platt, seedsman, of New Haven, and was carefully selected and freshly harvested.

When wheat flour or meal is made into a stiff dough with water and then carefully kneaded or squeezed in a gentle stream of water, the starch which makes up 60-68 per cent. of the flour or meal is gradually washed away for the most part, and there remains a tough elastic sticky mass.

The first published description of this body was made by Bec-cari in 1745 who gave it the name it still bears; *viz.*, *Gluten*.

In 1805 Einhof observed that hot alcohol extracts from wheat flour a substance resembling gluten. In 1820 Taddei showed

¹First printed in the Report for 1893 of the Connecticut Agricultural Experiment Station, New Haven; communicated by the author.

that gluten contains two substances, one soluble the other insoluble in boiling alcohol.

Since 1820 many chemists have undertaken to investigate gluten but their conclusions as regard the number, properties and composition of the proteids it contains, are extremely discordant. Einhof, Boussingault, Bouchardat, Denis, Weyl and Bischoff and Martin have considered gluten to consist essentially of a single proteid. Berzelius, DeSaussure, Liebig, Dumas, and Cahours, and Von Bibra, believed it to contain three, while Ritthausen and Bechamp regard it as composed of four proteids.

We have separated from the wheat kernel five distinct proteids; *viz.*, Gliadin, Glutenin, a Globulin, an Albumin and a Proteose. A proteose-like body, apparently distinct, was also obtained, but in too small quantity for satisfactory examination.

The mode of isolating these substances in a state of comparative purity and establishing their individuality, is fully stated in a former paper,¹ to which reference must be made for details.

Of these proteids only the first two properly belong to gluten.

I. *Gliadin* is the proteid which is readily dissolved from wheat flour and from gluten by hot dilute alcohol. It also exists in the rye-kernel.

This substance when dehydrated by absolute alcohol and thoroughly dried over sulphuric acid, forms a snow-white, friable mass which is easily reduced to a powder. If dried after being moistened with dilute alcohol or water it resembles, in appearance, pure gelatin. Dried thus, in thin sheets it is perfectly clear and transparent but is rather more brittle than gelatin. When treated in the cold with distilled water it becomes sticky and slightly dissolves. If the water is warmed, more dissolves and on boiling, much goes into solution. Solutions in warm water on cooling, deposit a part of the substance. The solution in pure water is instantly precipitated by adding a very minute amount of sodium chloride.

In absolute alcohol gliadin is entirely insoluble, but dissolves on adding water, the solubility increasing with the addition of water up to a certain point, and then diminishing. The exact degree of solubility for various strengths of alcohol has not been

¹ *Am. Chem. J.*, 15, 392.

determined, but mixtures of about seventy per cent. of alcohol and thirty per cent. of water dissolve the proteid in almost indefinite amount. From solutions in strong alcohol as well as from those in very weak alcohol the proteid is precipitated by adding a few drops of solution of sodium chloride, the completeness of precipitation depending on the strength of the alcohol and the amount of salt added. The more the alcohol varies in strength from seventy to eighty per cent. the more completely is the substance precipitated.

In extremely dilute acids and alkalies this proteid is readily soluble, and is precipitated from such solutions on neutralization apparently unchanged either in properties or composition.

Gliadin gives with Millon's reagent, with nitric acid and with the biuret-test, the usual proteid reactions. Dissolved in concentrated hydrochloric acid, a beautiful violet color develops slowly. With warm fifty per cent. sulphuric acid a similar color appears which is greatly increased in intensity on boiling.

On boiling its aqueous solutions, gliadin coagulates and becomes insoluble both in alcohol and in 0.2 per cent. potash solution, but is not thus converted into glutenin, the latter being soluble in weak alkali.

Gliadin was so called by Taddei because of its resemblance to glue. It has also been called plant-gelatin by Liebig, and glutin by Dumas. The plant-casein of Dumas, the mucin of De Saussure and Berzelius, the gluten-fibrin and wheat-mucedin of Ritthausen, are impure gliadin.

Gliadin is entirely distinct in composition from the alcohol soluble proteids of barley, maize, and oats. We found in Fife wheat, 4.33, and in Fultz, 4.25 per cent. of gliadin.

Our analyses of these gluten proteids are as follows:

| | Gliadin of wheat,
average of twenty-
five analyses. | Gliadin of rye,
average of thir-
teen analyses. | Glutenin of wheat,
average of eight
analyses. |
|---------------|---|---|---|
| Carbon | 52.72 | 52.75 | 52.34 |
| Hydrogen..... | 6.86 | 6.84 | 6.83 |
| Nitrogen..... | 17.66 | 17.72 | 17.49 |
| Sulphur | 1.14 | 1.21 | 1.08 |
| Oxygen | 21.62 | 21.48 | 22.26 |
| | <hr/> 100.00 | <hr/> 100.00 | <hr/> 100.00 |

II. *Glutenin.* Characteristic reactions of a proteid body which

can be dissolved only in dilute acids or alkalies are necessarily very few in number. Our preparations of glutenin after drying over sulphuric acid, were found to yield to distilled water, especially when warm, a little proteid substance. Diluted alcohol also dissolved a minute amount of proteid matter in the cold, and when heated to boiling, a much greater quantity. It is questionable whether the substance dissolved by water and by alcohol was not a trace of gliadin which had failed to be completely extracted in the process of preparing the glutenin. The fact that the solution in hot alcohol began to precipitate at once on cooling, and that especial care had been taken in every case to remove the gliadin, makes it probable that glutenin is slightly soluble in water and in alcohol, especially if these are warmed.

In very dilute alkalies, as 0.1 per cent. potash solution, and in very dilute acids, as 0.2 per cent. hydrochloric acid, glutenin, after dehydration with absolute alcohol and drying over sulphuric acid, is slowly soluble, with the exception of a greater or less amount of coagulated residue, depending on the circumstances of its preparation. When freshly precipitated, and in the hydrated condition, it is extremely soluble in the slightest excess of caustic alkali, and in a somewhat greater but still very slight excess of acid. In this condition it is also soluble in the slightest excess of sodium carbonate solution or ammonia. After drying over sulphuric acid it dissolves partly in 0.5 per cent. sodium carbonate solution.

Dissolved in concentrated hydrochloric acid it gives a solution slightly yellowish at first, but becoming a deep violet color on standing. In sulphuric acid diluted with an equal volume of water the solution is brownish in color after boiling, and remains clear when diluted. The undiluted solution, on standing, retains its brown color.

A comparison of the analyses of glutenin with those of gliadin shows a very close agreement of the two in composition. As it is well known that many proteids readily lose their solubility without change of composition detectable by analysis, it might seem proper to consider this body as an altered and insoluble gliadin.

There is, however, no evidence that gliadin is actually trans-

formed into glutenin, and since very recent investigation shows that rye-grain contains gliadin, but probably not glutenin, it would appear that the two are to be regarded as distinct.

This proteid, in an impure state, has been termed by various investigators zymom, plant-fibrin, gluten-casein, and gluten-fibrin. As all these names are associated with confused and erroneous notions as to its composition, origin, and properties, they are all properly discarded in favor of the new designation, glutenin.

In Fife wheat we found 3.96, and in Fultz, 3.91 per cent. of glutenin. The other proteids in the wheat kernel are—

III. *Edestin*,¹ a *globulin* belonging to the vegetable vitellins, soluble in saline solutions, precipitated therefrom by dilution, and also by saturation with magnesium sulphate, or ammonium sulphate, but not by saturation with sodium chloride. Partly precipitated by boiling, but not coagulated at temperatures below 100°. The wheat kernel contains between 0.6 and 0.7 per cent. of this globulin. When dried at 110° its composition was found to be as below stated.

IV. *Leucosin*,² an *albumin*, coagulating at 52°, unlike animal albumin in being precipitated on saturating its solutions with sodium chloride or magnesium sulphate. It is not precipitated on completely removing salts by dialysis in *distilled* water. It was found to form between 0.3 and 0.4 per cent. of the wheat kernel, and to have the following composition when separated from solution in the coagulated form by heating to 60° C.:

| | Edestin. | Leucosin,
coagulated. | Coagulum
from proteose. |
|----------------|----------|--------------------------|----------------------------|
| Carbon | 51.03 | 53.02 | 51.86 |
| Hydrogen..... | 6.85 | 6.84 | 6.82 |
| Nitrogen | 18.39 | 16.80 | 17.32 |
| Sulphur | 0.69 | 1.28 | } 24.00 |
| Oxygen | 23.04 | 22.06 | |
| | 100.00 | 100.00 | 100.00 |

V. A *proteose*, precipitated (after removing the globulin by dialysis, and the albumin by coagulation) by saturating the solution with sodium chloride, or by adding twenty per cent. of sodium chloride and acidifying with acetic acid. This body was

¹ *Edestin* edible.

² *Leucosin* white.

not analyzed in its unaltered form. On concentrating its solutions by boiling, a *coagulum* was gradually developed which formed about 0.3 per cent. of the wheat kernel and had the composition given above.

VI. The solution filtered from the substance just described (V.) still contained a *proteose-like body* which was not obtainable in a pure state. Its amount could only be roughly estimated by precipitating the concentrated filtrate from the preceding substance with alcohol, and multiplying the nitrogen contained in the precipitate by 6.25. The amount of this proteose was from 0.2 to 0.4 per cent. of the seed. Both this proteose and the above coagulum are unquestionably derivatives of some other proteid in the seed, presumably the proteose first mentioned.

The Formation of Gluten.—Wheat, as far as is known, is the only plant whose seeds contain proteid matter separable in a coherent form from the other constituents by washing with water. When ground fine and mixed with a suitable quantity of water it yields a dough from which a light, porous bread can be made. The importance of this fact in bread-making is so great that considerable attention has been paid to gluten by the chemists who have studied wheat proteids.

The investigations of Günsberg and of Martin, as well as our own, disprove the existence of gluten-fibrin and mucedin, which are currently stated to exist in gluten, and demonstrate that, as Taddei maintained, gluten consists of two proteids only.

Weyl and Bischoff have asserted¹ that the proteid matter of the wheat kernel is '*chiefly a globulin substance*, and that in contact with water it undergoes a change, presumably through the influence of a ferment, by which gluten is first produced.

The statements of these investigators are not sustained by any sufficient evidence. They say: "On investigating the proteids of wheat meal, one of us found principally a globulin substance, which he designated, in consequence of its similarity to myosin of the muscle, *vegetable myosin*. This vegetable myosin must be the mother-substance of the gluten, since in the wheat meal, together with it, other proteids, if at all, exist only in very small amount." What the reasons were for concluding that the

¹ *Ber d. chem. Ges.*, 1880, 367.

"myosin" constitutes nearly, if not all, the proteid of the wheat kernel does not appear. In view of our results this statement is certainly erroneous. Direct treatment of the meal with alcohol yields extracts containing gliadin in exactly the same amount as obtained from the gluten made from an equal quantity of flour, and extraction of either flour or gluten with alcohol, after complete exhaustion with sodium chloride solution, also gives the same proportion of gliadin. This substance must therefore exist in the seed, having the same composition and properties as in the gluten, and as it forms one-half of the gluten, it leaves the other half only as possibly derived from a globulin body through the influence of a ferment. If Weyl and Bischoff's view were correct, treatment of the flour with ten per cent. salt solution ought to alter the character and quantity of the gluten obtained, if not altogether to prevent its formation. This is not so, for the usual amount of gluten can readily be obtained from flour made into dough with ten per cent. sodium chloride solution, and then washed with the same until starch is removed.

Weyl and Bischoff next state that, "with the aid of a fifteen per cent. rock salt solution the flour was extracted until no proteid could be detected in the extract; the residue of the meal kneaded with water then gave no gluten. *If the globulin substance be extracted, no formation of gluten takes place.*" We have found that this is true if the flour is stirred up with a large quantity of salt solution, extracted repeatedly with fresh quantities of the same solution until no more proteid is dissolved, and the excess of solution removed by allowing the residue to drain on a filter as completely as possible. If, however, wheat flour is mixed at first with just sufficient salt solution to make a firm dough, this dough may then be washed indefinitely with salt solution, and will yield gluten as well, and as much, as if washed with water alone. This difference is due to the fact that when large quantities of salt solution are applied at once, the flour fails to unite to a coherent mass and cannot afterwards be brought together, as is possible when treated with smaller quantities of solution.

Weyl and Bischoff compare the formation of gluten to that of blood-fibrin from fibrinogen under the influence of a ferment.

They say that the formation of gluten is affected by all the conditions which interfere with the activity of ferments in general. "Large amounts of salt hinder the formation of gluten. Sulphates of magnesium and sodium behave like common salt." These statements are explained by what has been said above.

They tried unsuccessfully to obtain the supposed ferment in the following manner:

"We allowed meal with an equal weight of ninety per cent. alcohol to stand in closed vessels different lengths of time (in one case four months, then several times three to four weeks, frequently only eight to ten days). The vessels were repeatedly shaken and the yellow-colored alcoholic extract was poured off. The residue was freed from alcohol by pressing and evaporating at the ordinary temperature. After it was stirred up with water little or no gluten was obtained. Evidently the globulin substance had been coagulated for the most part by the alcohol." It is clear that if the flour were thus treated, the greater part of the gliadin would be removed. We have found that if flour be extracted with dilute alcohol until the gliadin is removed, and the residue freed from alcohol by exposure to the air, the latter will then yield no gluten when treated with water.

More recently Sidney Martin has advanced a somewhat similar theory of the formation of gluten from the proteids contained in the seed. He states¹ that alcohol extracts from gluten but one proteid substance; that this is soluble in hot water, but not in cold, and he therefore calls it an *insoluble phytalbumose*.

The residue of the gluten not dissolved by alcohol is uncoagulated proteid, if the alcohol has not been allowed to act too long. This substance he names *gluten-fibrin*. Martin further says that gluten dissolves almost completely in 0.2 per cent. hydrochloric acid, or 0.2 per cent. potash solution, leaving a small residue of fat. The solution gives a copious precipitate when neutralized, but the supernatant liquid still contains a quantity of proteid, which is the dissolved insoluble albumose. The whole of the gluten-fibrin is reprecipitated by neutralization, that is, it is wholly converted into an "albuminate."

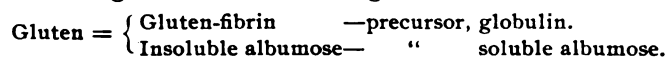
Martin then asks: "Does flour contain gluten-fibrin? Does it

¹ *British Medical Journal*, 2, 104, 1886.

contain insoluble phytalbumose?" The first question he says can not be answered directly. "The second is answered by extracting flour with seventy-six to eighty per cent. alcohol. This ought to contain the insoluble albumose if it were present as such in the flour, *but it does not contain it*; it extracts only fat." This statement is contrary to our experience, for we have never failed, in many experiments, thus to extract this substance (gliadin) from the flour, and that too in the same amount and of the same properties and composition as from the gluten.

Martin concludes that insoluble albumose is not present as such in the flour. He then says: "Before proceeding to mention its precursor, it will be well to state that ten per cent. sodium chloride solution extracts from flour a large quantity of globulin and of albumose. This globulin is of the myosin type, coagulating between 55° and 60° C., and precipitated by saturation with sodium chloride and ammonium sulphate. Both the globulin and albumose are present in a much smaller quantity in the watery extract of the flour." From this it is evident that Martin has fallen into the same error as Weyl and Bischoff, mistaking the albumin for a myosin-like globulin, and being greatly misled as to its amount.

Continuing, Martin says: "The direction of the evidence is to show that the insoluble albumose is formed from the soluble. Moreover, I think that the globulin is transformed into the gluten-fibrin, for I have been able to obtain from the globulin in solution a body having the same reactions as the gluten-fibrin." What this evidence is, which, by its direction, shows that the insoluble albumose is derived from the soluble, is not clear, and Martin makes no further statements on this point. That a body should be obtained from the solution containing the globulin which had the same reactions as the "gluten-fibrin" is not surprising, for the so-called "albuminates" derived from nearly all globulins have no characteristic reactions, being merely soluble in dilute acids and alkalis, and precipitated by neutralization in the same way as "gluten fibrin." Martin then states his theory of the formation of gluten in the following scheme:



This can not be a correct representation of the formation of gluten, for it has been shown to be founded on two erroneous observations: First, that alcohol does not extract proteid matter from the flour when applied directly, and second, that at least one-half the proteid matter of the seed is a myosin-like globulin.

The results obtained by us, and described at length in our paper,¹ lead to the conclusion that no ferment action is involved in the formation of gluten; that but two proteid substances are contained in the gluten, gliadin, and glutenin, and that these exist in the wheat kernel in the same form as in the gluten, except that in the latter they are combined with water in an amount equal to about twice the weight of the water-free proteids. The reasons for this opinion are, first, that alcohol extracts the same gliadin in the same amount, whether applied directly to the flour, to the gluten, or to the flour previously extracted with ten per cent. sodium chloride solution; second, that 0.2 per cent. potash extracts glutenin of uniform composition and properties from flour which has been extracted with alcohol or with ten per cent. sodium chloride brine and then with alcohol, as well as from gluten which has been exhausted with alcohol.

Both glutenin and gliadin are necessary for the formation of gluten, as shown by the three following experiments:

1. A portion of flour was washed completely free from gliadin by means of alcohol of 0.90 sp. gr., next with stronger alcohol, finally with absolute alcohol, and air-dried. The residue was then rubbed up fine until all lumps were removed, and water carefully added, and a dough made of the mass. A tolerably coherent dough was thus obtained, but much less elastic and tough than that produced from the untreated flour. This dough was then washed with water on a sieve, using every precaution to obtain a gluten, but none was formed.

2. Again, 7.5 grams of very finely ground air-dried gliadin were mixed intimately with seventy grams of fine corn-starch and distilled water added. A plastic dough was thus produced, but it had no toughness. On adding a little ten per cent. sodium chloride solution, the dough became at once tough and elastic. This was then washed with great care on a sieve with cold water,

¹ *Am. Chem. J.*, 15, 392-471.

a little ten per cent. salt solution being added from time to time, but in spite of every precaution no gluten was obtained.

3. The following experiment shows that the gliadin used was capable of forming gluten when glutenin was present, and also that salts have a marked influence on the toughness of wheaten dough.

Two portions of flour, weighing 100 grams each, were taken, and after adding five grams of gliadin to one, both were made into dough with the same quantity of water. The two doughs presented marked differences; that to which the gliadin had been added was much tougher and more yellow than the other. They were then washed with water as long as starch separated. The gluten was dried superficially by wiping with a cloth and weighed in the moist state. That from 100 grams of flour to which five grams of gliadin had been added weighed 44.55 grams; that from 100 grams of flour alone weighed 27.65 grams. The moist glutens were dried at 110° to constant weight, and both yielded the same proportion of dry gluten; *viz.*, 34.6 per cent. The yield of dry gluten was accordingly, in the first case, 15.41 grams, and in the second, 9.56 grams. The difference, 5.85 grams, shows that the added gliadin was fully recovered in the gluten.

The above figures show that these proteids combine with about twice their weight of water in forming gluten. The fact that the added gliadin entered so readily and completely into the formation of gluten indicates that it exists in the seed as such and undergoes no chemical change during extraction and drying.

The properties observed in testing the separated gliadin show how it acts in forming gluten, and explain many of the points observed by others and attributed to a ferment action.

When treated with distilled water in small amount the fine ground air-dry gliadin at once forms a sticky mass which, on adding more distilled water, dissolves to a turbid solution. If, however, a very little sodium chloride is added to distilled water and this applied to gliadin that has been first moistened with pure water, a very coherent, viscid mass results which adheres to everything it touches, and can be drawn out into long threads. If the gliadin is moistened with ten per cent. sodium chloride

solution and then treated with a larger quantity of this solution, the substance unites to a plastic mass which can be drawn out into sheets and strings, but is not adhesive. From this it is evident why Ritthausen, in washing flours which gave a fluid gluten, obtainable only in small quantity and with great difficulty, found that the addition of calcium sulphate to the wash-water rendered the gluten much more coherent and easily obtainable. The gliadin is thus proved to be the binding material which causes the particles of flour to adhere to one another in forming a dough.

But the gliadin alone is not sufficient to form gluten, for it yields a soft and fluid mass which breaks up entirely on washing with water. The insoluble glutenin is probably essential by affording a nucleus to which the gliadin adheres and from which it is not mechanically carried away by the wash-water.

It might be supposed that this insoluble glutenin, which so nearly resembles gliadin in composition, results from an alteration of the latter, brought about by the action of the mineral or other constituents of the seed or of the water. This is not probable, for the same amount of gliadin is extracted from flour directly by treating it with alcohol of 0.90 sp. gr., as is obtained from the gluten itself, and also the same amount is obtained after extracting the flour completely with ten per cent. sodium chloride solution, and then with alcohol.

The behavior of the gliadin towards ten per cent. sodium chloride solution shows why no gluten was obtained by Weyl and Bischoff from flour extracted with this solvent. The gliadin had under these conditions no adhesive qualities, and therefore was unable to bind the flour into a coherent mass. If, however, the salt solution is added in small quantities, and the flour kneaded and pressed, the particles are brought together and then adhere tenaciously.

DEGRAS.¹

BY CHARLES S. BUSH.

IN this country, the term "degras" is generally applied to the grease or fatty matter recovered from the water in which wool has been scoured; in various portions of Europe, the term

¹ Read before the Rhode Island Section, January 23, 1894.

is employed not only in connection with grease extracted from the waste-water of wool-washing establishments, but also to designate the oil or fatty matter recovered at chamois-skin manufactories.

It is my intention at this time to call your especial attention to *degras* of the first named type, which, I may say, has but one source; namely, the water in which wool has been scoured.

The process of producing or manufacturing *degras* (or so-called wool grease) is, comparatively speaking, a simple one and may be described as follows: The soapy liquid remaining in the scouring tubs or machines, after the wool has been scoured, is run off into a large shallow tank or pond and allowed to settle; the greater portion of the grease rises to the surface, but more or less adheres to the dirt and other foreign matter and is carried to the bottom. From time to time, the material which has accumulated at the bottom of the tank or pond is removed, and the grease, or a large portion thereof, is recovered. After the settling process is completed, the liquid is pumped into tanks and allowed to stand for a few days. The next step in the process is to add sulphuric acid. This withdraws the alkali used for washing the wool and breaking up the soapy emulsion, causes the grease and water to separate (this is commonly called "cracking the grease"). The contents of the tanks are then transferred to filter beds where the water is allowed to drain off, the grease and sediment being left behind in the filters. The filter beds may be composed of sawdust or other suitable material. The substance remaining in the filters is then transferred to pieces of bagging and shaped into flat packages. A large number of these packages are placed in power presses and steam applied in order to raise the temperature sufficiently to cause the grease to ooze out and flow into tanks provided for the purpose. Any water which may find its way into the presses will naturally pass into the tanks with the grease, but separation takes place at once and the hot *degras*, forming a layer on top, is readily drawn off into the barrels. After the *degras* has been allowed to cool, it is of about the consistency of soft tallow, and in such form is ready for market.

The color of the substance under consideration is yellowish-

brown; it has a disagreeable odor which is not easily described. This odor is due to two causes; first the presence of foreign substances, as dung and urine products, which are still present while the grease is being melted; second, the presence of certain volatile fatty acids which were present as potash salts in the wool, and, being soluble in the grease, remain with it after treatment of the emulsion with strong acid.

The individual character is given to wool grease by an interesting substance called cholesterin, the chemical formula of which is $C_{27}H_{48}O$. This substance is soluble in hot alcohol but precipitated in cold, in the form of tabular crystals somewhat resembling silver nitrate. As the extracted wool grease does not precipitate in the crystalline form, I think it is fair to infer that the cholesterin exists in the wool fat chemically combined with the fatty acid, and not in a state of mixture. Cholesterin is not saponifiable but it makes a most perfect emulsion, taking up 120 per cent. of water and remaining in that emulsive state for years; a sample in my possession is three years old and still shows no signs of separating.

Degras finds its chief use in the finishing of leather, superseding tallow for that purpose to a great extent, on account of the low price of the former and because of its penetrating and emollient nature. Degras is used to some extent in the manufacture of wool-oils, rope-oils, etc. Many persons have been led to believe that this waste material, which has polluted our streams and formed a subject for much discussion, is used extensively in the manufacture of soap. Some months since, an article appeared in one of our local newspapers from which I quote the following words: "In regard to finding a market for this material, I think it possible to sell it to almost any soap manufacturer. A large business is done in New York in this, and at a price of 2 to 2½ cents per pound." To say the least, this newspaper statement is misleading. Degras has been used to a slight extent by a few soap manufacturers but the results have been anything but satisfactory. Cholesterin is unsaponifiable and a positive injury to the soap. It has no deterative properties and is undesirable as a "filler." There is no doubt that new outlets for this interesting product will be discovered eventually.

THE BORIC ACID WORKS AT LARDARELO.¹

BY WM. P. MASON.

SO far as I am aware no recent description of these famous works has been given, and there is certainly wide-spread ignorance as to the best route by which to visit them. The most convenient starting point is Pisa, whence a train may be taken for Cecina at 6.10 A. M.

At Cecina one must change cars for the branch line going to Volterra. At Volterra station (not the town of that name, which lies some five miles away) a comfortable one-horse wagon, holding two besides the driver, may be hired for the round trip for ten francs. The regular post is to be avoided as it does not go far enough. The drive to Lardarelo will take two and a half hours, and the return journey will take about the same time. An evening train leaves Volterra station for Pisa. An attempt to pass the night *en route* would be attended with discomfort and is not recommended.

Unless the visitor be able to speak Italian an interpreter would be absolutely necessary.

The scenery between Volterra and Lardarelo, although hilly, can hardly be termed mountainous; and the soil, though poor in quality, is cultivated, olive plantations being seen in plenty. Altogether, the description of the approaches to the place, as depicted by the older authors, savors of a much more grim locality than the valley seen by the traveler of to-day—its infernal characteristics sink into nothingness when compared with the Yellowstone Park.

The dark color of the masses of friable serpentine on the hillsides, during the last mile of the drive, is the only reminder of the scenery as described by Muspratt, but wherever this rock occurs it does certainly give the surroundings "the appearance of having been burned."

Upon crossing a ridge within half a mile of the end of the journey, the boric acid plant, and its attendant village, suddenly come into view, and, with the numerous jets of native steam

¹ Read at the Baltimore Meeting, December 28, 1893.

rising from and among the buildings, the resemblance is very strong to a busy New England factory town.

All of the district now covered by the works was originally owned by the people of the neighboring ancient town of Monte Cerboli, but having been held by them as of little value, it was very cheaply obtained in 1818 by a poor young Frenchman (grandfather of the present Count Lardarel) who detected the presence of boric acid in the steam and who was shrewd enough to appreciate the value of his discovery.

He at first formed a company for the purpose of developing the property, but later acquired entire possession himself.

The boric acid, to the extent of one-tenth of one per cent., is contained in the native steam that issues from the earth through numerous orifices, all of which have been tubed to a greater or less degree.

These tubings are mostly of eight-inch pipe, and extend into the earth varying distances, some a few feet and others over three hundred. Certain of the fumaroles are entirely artificial, having been bored after the manner of artesian wells. The boring tool, when it reaches the steam zone, usually drops suddenly a yard or more, and immediately thereafter steam escapes with much force. The temperature of the issuing steam varies in the different outlets from 98°-140° C., and it rushes from the pipes with great noise and power.

Ordinary spring water is led into a circular brick cistern about thirty feet in diameter, and an eight-inch pipe, conducting natural steam passes through the cistern wall about one foot below the water surface.

The issuing steam, which impregnates the water with boric acid, causes a fountain of several feet in height to play in the cistern.

After an interval of twenty-four hours the contents of this cistern are piped into another similar one on a lower level, and are then subjected to a further injection of steam for an additional twenty-four hours, after which the solution passes to a square settling basin where a grayish mud, of exceedingly fine state of division, separates.

This mud, which contains more or less boric acid, is given

away to the country people who use it as an application for diseases of the hide occurring among sheep and cattle.

From the settling tank the boric acid water passes to evaporating pans (forty in number) made of lead. These pans are six feet wide, 150 feet long, and eight inches deep. They are slightly inclined, and are divided by small ridges two and a half inches high crossing them transversely every two feet. The liquid enters at one end and slowly flows over the step-like divisions to the other, the rate of inflow being made equal to that of evaporation.

When, in the judgment of the attendant, the concentration has been carried far enough, the flow is cut off and the hot, concentrated liquor is brushed out by brooms into crystallizing tanks, ten by thirty feet in size, and allowed to cool.

The deposited crystals of boric acid are removed by wooden scoops, drained in baskets, and the mother liquor is returned to the evaporating pans.

The crystals are spread upon a steam-heated drying floor protected by a shed-like building thirty by fifty feet in area, and when dry are placed in bins for storage. Shipment is made in casks holding about 1,000 pounds each. The heating of the evaporating pans and drying floor, in short heating of every description throughout the establishment, is by native steam.

About 200 hands are employed in the works, and the annual output is approximately 1,700 tons, all of which is shipped to England, *via* Leghorn.

Count Lardarel appears to have a careful eye for the welfare of his employees, as is evinced by the substantial manner in which the village is built, its cleanliness and the attempts made to adorn the streets. He was awarded a medal at the Paris Exposition for his contributions towards the betterment of social conditions, in addition to an award made for his manufactures.

The statement in our standard works of reference that "boric acid is recovered at both Monte Cerboli and at Lardarelo," is confusing, as they are practically one and the same place; and the dimensions given the artificial lagoons, "100 to 200 feet in diameter," is a great exaggeration.

THE COMMERCIAL VALUATION OF LEAD-TIN AND LEAD-ANTIMONY ALLOYS.¹

BY JOSEPH W. RICHARDS, PH.D.

LEAD-TIN alloys are used principally as soft solders, for coating terne plates and making "tin-foil." The amounts used annually for these purposes in this country may easily amount to twenty or thirty thousand tons, valued at some five million dollars. Since lead is worth about five cents a pound, and tin about twenty, the percentage of the latter fixes the value of the alloy; and since dishonest manufacturers are constantly trying to "cut grades" by shaving down the proportion of tin, consumers are constantly on the alert to detect such frauds. A quick, easy method of determining approximately the percentage of tin in such alloys becomes a valuable desideratum in such important industries. Accuracy to one per cent. is amply sufficient for all commercial purposes, because alloys conscientiously made by a careful manufacturer will vary that much from what they are intended to be if made by simply mixing given weights of the two metals.

Lead-antimony alloys, or hard lead, run up to twenty-four per cent. of antimony. Many thousand tons of this is used annually in the type-metal and britannia-ware industries, the proportion of antimony varying usually between five and fifteen per cent.

The commercial testing and valuation of such alloys can be most conveniently and quickly accomplished by determining their specific gravities. Pure lead has a density of 11.33, pure tin 7.43, and antimony 6.65. When tin is added to lead, the density at once falls; not uniformly, however, and the alloy, furthermore, does not have a density such as could be calculated from that of its component metals. It is the same on adding antimony, except that with one per cent. the alloy is *heavier* than lead, with two per cent. it is just the density of lead, and above that figure the gravity decreases as with tin. Over twenty-four per cent. of antimony, no homogeneous alloy can be obtained, and this sets a limit to the specific gravity tests; however, twenty

¹ Read before the Lehigh Valley Section, May 3, 1894.

542 VALUATION OF LEAD-TIN AND LEAD-ANTIMONY ALLOYS.

per cent. may be regarded as the maximum ever found in commercial "hard lead."

To inaugurate this scheme of testing, it is necessary to carefully make the whole series of alloys, every one or two per cent. from pure lead to pure tin, and from pure lead up to twenty-four per cent. of antimony. Having determined the specific gravity of these alloys by the time-honored scheme of weighing in air and water, with a good balance, the results are tabulated, and any commercial alloys similarly treated and referred to it are at once identified. This method, however, requires a delicate balance and a careful operator; in fact, rather more skill than an ordinary metal-handler possesses. The apparatus shown



in the accompanying cut was devised by Mr. Joseph Richards, of the Delaware Metal Refinery, Philadelphia, to facilitate these tests. The idea is to cast a bullet of fixed size in a brass mould, with each of the standard alloys, and then to weigh the bullets on a delicate scale. The scale shown has agate bearings, and the long beam is graduated every one per cent. from 0-pure lead, to 100-pure tin. On the reverse side, the beam is graduated from two up to twenty-four for the lead-antimony alloys. The marks on the beams have all been fixed by placing on the pan successively bullets of the standard alloys, and marking their weight.

The operation of testing a lead-tin or "hard lead" alloy thus resolves itself into simply melting it in a small iron ladle, pouring

the bullet and placing it on the scale; on balancing, the percentage of tin or antimony is read off directly on the beam. The balance is delicate enough to rise or fall with a movement of less than one-half of one per cent., while, with care, duplicate bullets may be cast not varying in weight over one-half per cent. The only precautions to observe are to continue the pouring until the bullet is set, in order to avoid a shrinkage cavity, and not to pour into a hot mould, which would necessarily be larger and cast a heavier bullet. The whole operation of melting, casting, and weighing can be performed easily in three to five minutes, and, if need be, by any workman of ordinary intelligence.

Nearly a score of these outfits have been sold by Mr. Richards during the last six months, and their introduction into the industries using these alloys has displaced the rule-of-thumb practice by accurate calculation, and brought many a dishonest manufacturer to his proper deserts.

PYROXYLIN, ITS MANUFACTURE AND APPLICATIONS.¹

BY WALTER D. FIELD.

PART III.

(Continued from p. 498.)

THE peculiar form in which pyroxylin is deposited from its ether-alcohol solution, first called the attention of experimenters to it as a means for producing improvements in the various industrial arts. Photography was the first of the industrial arts to utilize this peculiar property of soluble nitrocellulose.

Later English experimenters made attempts to use pyroxylin as the base for an imitation bone, ivory or hard rubber. Parks, Spill, Greening, and others labored industriously to find some way or some solvent that would dissolve pyroxylin so they could obtain it in solid blocks suitable for turning and molding.

Four years after Scott Archer used pyroxylin in photography, Parks filed his first patent for the use of a solution of pyroxylin. (Eng. Pat. No. 2359, Oct. 22, 1855.) Then again in May, 1858 (Eng. Pat. No. 1090), John MacIntosh proposed the use of pyroxylin dissolved in a solvent composed "of equal parts of wood spirit and coal naphtha" for use in the insulation of wire. In 1864 Parks (Eng. Pat. No. 2675) proposed the use of pyroxy-

¹ Read before the World's Congress of Chemists, June, 1893.

lin with gum ballata and says: "I employ as a solvent which I prepared by distilling wood naphtha with calcium chloride." Parks seems to recognize the desirability of using a solvent as near anhydrous as possible, and says the greater the quantity of calcium chloride used the stronger the solvent. But because of his solvent Parks was unable to make his experiments successful, and so he begins to search for solvents that would not evaporate so quickly and would enable him to work the pyroxylin solution in heated rolls. Parks finds that nitrobenzene, aniline, glacial acetic acid, and camphor dissolved in the more volatile solvents, methyl alcohol and alcohol-ether are much better for use in producing a plastic as they are less volatile and develop greater solvent action under the influence of heat.

Spill (Eng. Pat. No. 3102, 1869) finds camphor in alcoholic solution, camphor oil, aldehyde alone or with alcohol, solvents of pyroxylin. Ethyl and methyl acetates were found to be solvents of pyroxylin by Pelouse (*Compt. rend.*, **24**, 2), and ether-alcohol by Dominte and Merard (*Compt. rend.*, **29**, 390). Acetone was known to be a solvent of pyroxylin prior to 1864. To the solvents already given none were added until 1882, when John H. Stevens took out a series of patents, in which he gives a large number of new solvents for use in the production of solid compounds of pyroxylin. In these patents (U. S. P. Nos. 269,340, 269,341, 269,342, 269,344, 269,345,) he names the following substances: methyl nitrate, ethyl butyrate, ethyl valerate, ethyl benzoate, ethyl formate, methyl salicylate, amyl formate, amyl acetate, amyl butyrate, amyl valerate, ethyl sebacylate, ethyl oxalate, diamyl oxide, which are all active solvents of pyroxylin, that is they are solvents at the usual temperatures. He names dinitrobenzene and coumarin as latent solvents, that is, they are solvents at their melting points or when dissolved in alcohol. Stevens also finds acetal, amyl nitrate, and amyl nitrite in alcoholic solution to be solvents of pyroxylin at ordinary temperatures.

In 1889 Robert Shupphous took out a series of patents (U. S. P. Nos. 410,204, 410,205, 410,206, 410,207, 410,208, and 410,209). He finds propyl and isobutyl alcohols with camphor active solvents, and the ketones, palmitone, and stearone in

alcoholic solution, also alpha and beta naphthol with alcohol, and anthraquinone (diphenylene diketone) in alcoholic solution. Iso-valeric aldehyde and its derivatives, amyliden-dimethyl and amyliden-diethyl ethers, Shupphous finds are active solvents of pyroxylin.

In 1892 August Sayer (U. S. P. No. 470,451) informs us that diethylketone, dibutylketone, dipentylketone, and the mixed ketones, methylethyl, methylpropyl, methylbutyl, methylamyl, and ethylbutylketones are active solvents of pyroxylin. Still later Leonard Paget (U. S. P. No. 494,793) finds that methylamyl oxide is a solvent but ethylamyl oxide (U. S. P. No. 494,792) is not a solvent.

The solvents of pyroxylin can be divided into the following general classes: First, those which are solvents, without the aid of heat or solution in alcohol; second, those that are solvents when dissolved in alcohol. These solvents are those which also develop a solvent action when heated to their melting point in combination with pyroxylin.

We also find that chemically the solvents of pyroxylin can be grouped into classes as follows: Two of the monohydric alcohols; compound ethers of the fatty acids with monohydric alcohols; aldehydes; simple and mixed ketones of the fatty acid series. These classes include the greater number of the solvents of pyroxylin those not included are as follows: Amyl nitrate and nitrite, methylenedimethyl ether, ethidenediethyl ether, amyl chloracetate, nitrobenzene and dinitrobenzene, coumarin, camphor, glacial acetic acid, and mono, di, and triacetin.

Another division of the solvents of pyroxylin is necessary when we consider their properties. We find it necessary to divide the solvents of pyroxylin into two great classes according as they are hygroscopic or non-hygroscopic. To the first class belong acetone, methyl acetate, ethyl acetate, methyl alcohol, aldehyde, ethyl formate, propyl formate and acetate. These solvents when they deposit pyroxylin from their solution, also absorb water and this precipitates the pyroxylin in the form of a white cloud on the surface of the deposited film. In some cases this cloudiness extends entirely through the film and it is like chalk dust in appearance.

Dr. Guido Wolfram (*Dingler's Poly. J.*, 230, 156,) says: "Pentanitrocellulose is soluble in acetone, acetic ether, and still easier in a mixture of the same with ethyl ether. The solution gives a cloudy layer (matte) or film on evaporation." The pentanitrocellulose was not the cause of the cloudy film, for if he had used anhydrous solvents and evaporated his solution in a chamber free from moisture he would have obtained clear films.

Wolfram says: "The solution of the tetranitrocellulose in acetic ether, acetone, and wood-spirit, wood-spirit ether, acetic ether, ether, and acetone ether, gave a hazy opaque layer—a proof that the obtaining of a vitreous layer depends not only on the substance but likewise on the kind of solvent used." If Wolfram had used alcohol instead of ether in combination with the hygroscopic solvents he would have obtained clear transparent or glassy films on the evaporation of the solvent by reason of the alcohol absorbing the water and preventing the precipitation of the pyroxylin.

All the non-hygroscopic active solvents of pyroxylin deposit it from solution as a transparent, glassy film.

The action of the various solvents towards pyroxylin is often very peculiar. Thus is the case of the alcohol-ether solvent, neither the ether nor the alcohol is a solvent yet when combined they produce an active solvent. Camphor when dissolved in alcohol produces a good solvent; on the other hand camphor dissolved in the ketones reduces their solvent action. Nitrobenzene gives a solution that is granular, it seems to merely convert the pyroxylin and not to dissolve it, on the addition of alcohol (distilled from lime) we have at once a solution, that is, the granular appearance disappears and the solution becomes homogeneous.

The acid mixture and the method of nitrating has much to do with the action of the various solvents. The influence of water (uncombined) in the acid mixture, the influence of the immersion temperature, and the effect of increasing the nitric acid and diminishing the sulphuric acid, all influence the solubility of the resulting product.

We will consider first the influence of mechanically mixed water on the solubility of the pyroxylin.

Starting with a mixture of eight pounds of nitric acid, sp. gr. 1.435, and sixteen pounds of sulphuric acid, sp. gr. 1.83, and one-twentieth part by weight of cotton, first add six ounces of water and immerse the cotton at 60° C. The cotton is finished in ten or twelve minutes, and when washed and dried is found to be very pulverulent, or rotten and dusty, and occupies a much smaller bulk than the non-pulverulent variety insoluble in methyl alcohol. This pyroxylin is very soluble in methyl alcohol and in all hygroscopic solvents, giving with them limpid thin solutions.

Again taking the same proportions of acids of the gravities as given above, and the same amount of cotton for nitration, and adding nine ounces of water, the temperature of the immersion this time being 65° C., we find the pyroxylin produced very much more soluble in methyl alcohol than that produced by the first formula. Also that all its solutions are more limpid or fluid.

In this formula we have the following amounts of water: Eight pounds nitric acid, sp. gr. 1.435, contains 2 pounds, $2\frac{2}{3}$ ounces water. Sixteen pounds sulphuric acid, sp. gr., 1.83, contains 1 pound, $1\frac{2}{3}$ ounces water. Nine ounces water added makes the total water in the acid mixture 3 pounds, $13\frac{8}{15}$ ounces.

Now if we took a weaker nitric acid that would contain the desired water, without addition, as in the following formula: Eight pounds nitric acid, sp. gr. 1.40, contains 2 pounds, $10\frac{4}{5}$ ounces. Sixteen pounds sulphuric acid, sp. gr. 1.83, contains 1 pound, $1\frac{2}{3}$ ounces. Giving a total of 3 pounds $12\frac{8}{15}$ ounces. We would naturally suppose that this formula, containing as it does within an ounce of the same amount of water as the first formula, would produce pyroxylin having almost identical solubilities with that produced by the first formula. The two formulas do not, however, produce pyroxylin having the same solubilities, using, of course, in nitrating, the same temperature.

The pyroxylin produced by the formula containing the mechanically added water, is very soluble in methyl alcohol and hygroscopic solvents, but only imperfectly soluble in non-hygroscopic solvents, for instance, the compound ethers. Whereas the pyroxylin produced by the second formula, containing no mechanically added water, is perfectly soluble in the non-hygroscopic solvents, and its solutions in the hygroscopic solvents

are inclined to be heavy. The nitric acid used in these experiments was water-white and free from any dissolved nitrogen oxides.

The pyroxylin made from the formula containing the mechanically added water yields a film that is very contractile, that is, when it is deposited from its solution on a piece of plate glass it differs from other pyroxylin in drying to a much smaller bulk.

It was, however, the fact that the non-hygroscopic solvents of pyroxylin would deposit it as a film having great strength and transparency that led to its use for producing a varnish which could be applied to brass and silverware by simply dipping articles in it. The person who practically applied these properties was Richard Hale (U. S. P., No. 471,422). Hale uses the following solvent: Amyl acetate, four volumes; petroleum naphtha, four volumes; methyl alcohol, two volumes; pyroxylin, four to five ounces to the gallon of solvent. In this case, Hale has used petroleum naphtha to hasten the drying qualities of the varnish, so that it would set on the article to be varnished before it had a chance to run off. It was, however, the non-hygroscopic character of the solvent that made the varnish successful when it came to practical application. This very formula, or one which is a very slight modification, is used to-day in the production of thousands of gallons of pyroxylin varnish.

The varnish made on this principle is also used for varnishing pens and pencils and it gives them such a superior finish that they command a higher price than those varnished with the ordinary varnish.

And now the last industry that has sprung up, because of the wonderful properties of pyroxylin when deposited from its solution in a non-hygroscopic solvent, is the production of photographic films, flexible glass we would call it, and really, what better name could we give it? Henry Reichenbach made the first application of the use of a solvent of pyroxylin, that was practically non-hygroscopic, to the production of a photographic film. In his patent, issued in December, 1889, Reichenbach gives a formula, but as this formula is no longer in use, from the fact of its being too largely composed of hygroscopic solvents, there is no need of producing it here. It has been due to the recognition

by experimenters, that by a suitable combination of solvents solutions could be produced that would flow fast or slow, set rapidly or slowly, and produce the varied products desired, that the industry has developed so rapidly.

Hyatt's discovery that a mixture of camphor and pyroxylin when heated could be worked like rubber was the beginning of the success of the celluloid industry. Hyatt discovered the latent solvent action of camphor.

RECENT WORK ON THE SUGARS.

By B. B. ROSS.

Received May 24, 1894.

THE ESTIMATION OF INVERT SUGARS.

Bauman (*Ztschr. des Ver. f. Rubenzucker Ind.*, 42, 824) gives a new table, based upon the original table of Herzfeld, for the calculation of invert sugar percentages in solutions containing considerable proportions of sucrose. The table is quite similar to that of Herzfeld, but provides for the employment of only five grams of material instead of ten grams, as in the old table.

Ehrmann (*Bull. Assoc. Chim., France*, 10, 537) describes a method for the indirect gravimetric estimation of glucose by means of the reduction of one of the double platinum chlorides by the copper suboxide thrown down by the invert sugar.

The suboxide, precipitated in the usual manner is brought upon the filter and washed thoroughly; the reduction of the precipitate is next effected by pouring upon the filter a small amount of a concentrated solution of potassium platino or sodium platino-chloride, the red precipitate of suboxide being superseded by a black deposit of platinum.

After washing and igniting the residue, the amount of invert sugar corresponding to the weight of platinum obtained, can be readily calculated.

The author claims that this method is more rapid and easy of execution than the reduction of cuprous oxide in a current of hydrogen, and that it is also more exact, for the reason that the atomic weight of platinum is much higher than that of copper.

Nihoul (*Chem. Ztg.*, 17, 500) refers to the gravimetric

method dependent upon the reduction of the copper suboxide in a current of hydrogen, and offers the objection that the process, though accurate, is both tedious and time-consuming.

The process of Holdefleiss, involving the oxidation of the cuprous to cupric oxide with nitric acid, is also noted, as well as the objection of Soxhlet that a loss occurs from the formation of basic copper nitrate and that an error is occasioned by the retention of copper in the filters. The author reports results of tests refuting the first claim of Soxhlet and recommends the employment of double filters in order to obviate the slight error resulting from the presence of the small amount of copper retained in the filter papers. The inner filter containing the precipitate, and the outer filter are separately treated with nitric acid, ignited and weighed, the differences in the weights secured giving the weight of cupric oxide, and this multiplied by the factor 0.889 gives the amount of cuprous oxide corresponding thereto. From this the proportion of glucose can be readily obtained by reference to Allihn's tables.

Blank experiments with double filters showed that practically the same amounts of copper solution were absorbed and retained by each filter.

On account of the passage of small quantities of the suboxide through the first filter (as sometimes happens), it is recommended that quadruple filters be employed, the filters being ignited and weighed in pairs instead of individually.

By the observance of these directions, it is claimed that satisfactory results can be quickly and easily secured.

The author also reports the result of experimental tests of the gravimetric method which provides for the bringing of the suboxide upon tared filters, drying and weighing.

Two sets of double filters were employed in the filtrations, and in order to determine whether or not oxidation of the precipitate occurred during the drying process, some of the precipitated suboxide was maintained at a temperature of 75°–100° C. for two days without perceptible variation in weight.

It was found on investigation, however, that the precipitate obtained did not correspond precisely, in composition, to the formula Cu_2O , being contaminated to a slight degree with organic matter.

In following this method, which in other particulars is said to be highly satisfactory, it is therefore necessary to make a correction for the proportion of organic matter contained in the precipitate, this correction being generally about 0.3 to 0.4 per cent. of the weight of the cuprous oxide.

INVERT SUGARS IN THE BEET.

Classen (*Deutsche Zucker, Ind.*, 1893, *Sucr. Ind.*, 41, 242) recommends that in the estimation of invert sugars in the beet, the juice obtained by pressure from the beet be not employed and that, instead, the direct aqueous method of extraction be used in the preparation of the solution required for the determination.

For this purpose, the warm digestion process is found advantageous, a small amount of lead subacetate and precipitated calcium carbonate being previously added. Excess of lead subacetate should be avoided since this leads to the destruction of invert sugars, and on the other hand, if the juice has an acid reaction, inversion of sucrose will take place; the acidity, however, can be readily corrected by the employment of calcium carbonate.

The process recommended is as follows: Take 110 grams finely divided chips, add ten to fifteen cc. lead subacetate solution and one to two grams of precipitated calcium carbonate, digest in a half-liter flask on a water-bath from three-quarters to one hour. After cooling and making up to the mark, the moderately clear juice is decanted off and 100 cc. of it is measured out; a small amount of lead subacetate is next added to complete the clarification and the solution made up to 110 cc. and filtered. To 100 cc. of the filtrate a small amount of soda solution is added to precipitate the lead and the volume is then brought up to 200 cc. One hundred cc. of this liquid corresponds to ten grams of the beet pulp, and after its filtration, the reduction of Fehling's solution can be accomplished in the usual manner.

LEAD SUBACETATE FOR CLARIFICATION.

Courtonne (*Bull. Assoc. Chim., France*, 10, 457) refers to the chief methods proposed for the preparation of lead subacetate solutions and to the various formulas which have been assigned to this salt.

A series of tables is presented, giving densities of solutions of neutral and basic acetate, with the proportions of the solid salt, lead oxide and acetic acid contained therein, and showing also the relations between the two classes of solutions with reference to the amounts of acid and base present.

The author proposes the preparation of a basic acetate solution by adding to a solution of the neutral salt, an amount of ammonia sufficient to combine with such a proportion of the acetic acid of the lead acetate as will result in the formation of lead subacetate in solution along with ammonium acetate.

The proportions of the substances employed in the preparation of this solution are as follows:

| | |
|--|------------|
| Crystallized neutral lead acetate..... | 350 grams. |
| Distilled water..... | 825 " |
| Ammonia (22°)..... | 55 " |

The author states that this solution has been employed by him for a long period of time and has given uniformly good results in the clarification of sugar solutions.

In addition to the tables above referred to, the author inserts an additional one giving data of a corresponding character for solutions prepared by the process just described.

THE INFLUENCE OF LEAD SUBACETATE, UPON THE POLARIZATION OF CANE JUICES.

Saillard (*Bull. Assoc. Chim., France*, 10, 354) reports results of a number of polariscopic tests of cane juices, where both normal and basic lead acetate were employed in the clarification.

Where the subacetate was employed the results were considerably higher owing to the formation of insoluble lead levulosate, thus decreasing the normal levo-rotary influence of the invert sugar present.

The author gives examples showing the effect of this difference upon the aggregate results for a whole milling season.

[Note by abstractor—Attention was called to this point a number of years since by Gill, Spencer, Edson, and others.]

THE INFLUENCE OF ALKALINE NITRATES UPON THE POLARIZATION OF SUGAR SOLUTIONS.

Gravier (*Bull. Assoc. Chim., France*, 10, 351) reports a number of experiments which he has conducted in order to ascertain

the influence of alkaline nitrates upon the polarization of sugar solutions. The tests were executed with both aqueous and alcoholic solutions, and both in the presence and absence of lead subacetate.

In aqueous solution the influence of potassium and sodium nitrates was almost inappreciable, but in alcoholic solutions, in the presence of lead subacetate, there was quite a considerable diminution in the polariscopic readings.

The author concludes that it is inadvisable to employ alcohol as a solvent in polariscopic work, especially where lead subacetate is used.

[TO BE CONTINUED.]

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE.]

THE VOLUMETRIC DETERMINATION OF PHOSPHORUS IN STEEL.¹

BY W. A. NOYES AND E. D. FROHMAN.

Received June 18, 1894.

VERY full directions for the volumetric determination of phosphorus in steel have been recently given by C. B. Dudley and F. N. Pease.² The method is rapid and easy of execution and gives concordant results in the hands of careful workers. There is, however, an uncertainty of about ten per cent. as regards the factor which should be used for converting the iron equivalent of the permanganate solution into the phosphorus equivalent. The most careful determination of the character of the products obtained by reducing molybdic anhydride with zinc and sulphuric acid seems to be that of v. der Pfordten,³ who finds that when solutions are reduced and titrated with but slight exposure to the air the molybdenum is reduced to a form corresponding to the oxide Mo_2O_3 . If this is true one molecule of molybdic anhydride requires, after reduction, the same amount of oxygen for oxidation as three atoms of iron. If we assume, further, that the yellow precipitate contains twelve molecules of molybdic anhydride for one atom of phosphorus, it follows that

¹ The work here described was presented to the Faculty of the Rose Polytechnic Institute for the degree of Bachelor of Science by E. D. Frohman.

² *J. Anal. Appl. Chem.*, 7, 108. This JOURNAL, 15, 519.

³ *Ann. Chem.*, (Liebig) 222, 155.

one atom of phosphorus is equivalent to thirty-six atoms of iron. The iron equivalent of the solution should, therefore, be multiplied by $\frac{81}{86 \times 66}$, or by 0.01538, to find the phosphorus equivalent.

Werncke,¹ however, claims that the molybdenum is reduced to a form corresponding to the oxide $\text{Mo}_{12}\text{O}_{10}$. This would give the factor 0.01628.

Blair² follows Werncke and gives factors which reduce to the one last given.

Dudley and Pease³ assume the same ratio between molybdic anhydride and iron but a different and empirical ratio between phosphorus and molybdic anhydride. Their factors combined give the factor 0.01724.

Doolittle and Eavenson⁴ give factors which, when reduced to the same form, give the factor 0.0160.

These facts led us to take up a study of the question in order to determine, if possible, the cause of the differences and what the true factor is.

We undertook first the determination of the form to which the molybdenum is reduced. For this purpose we intended to use known amounts of pure molybdic anhydride. On examining the molybdic anhydride on hand, which had been bought as chemically pure, we found that it contained considerable quantities of ammonia and also some sodium. On account of the difficulty of preparing the anhydride in pure condition we determined next to use sodium molybdate. This was prepared from the anhydride by dissolving in the calculated amount of sodium hydroxide and crystallizing the salt obtained from water. When dried over sulphuric acid *in vacuo* the salt contains two molecules of water of crystallization. This is completely expelled at 250°.

0.5713 gram of the salt lost 0.0823 gram H_2O at 250°.

0.1710 gram of the salt lost 0.0249 gram H_2O at 250°.

| Calculated for $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$: | | Found. | |
|--|-------|--------|-------|
| | | I. | II. |
| $2\text{H}_2\text{O}$ | 14.88 | 14.40 | 14.56 |

¹ *Ztschr. anal. Chem.*, 14, 9.

² "Chemical Analysis of Iron," first edition, p. 86.

³ This JOURNAL, 16, 230.

⁴ Ibid, 16, 243.

The purity of the dry salt was further established by determining the amount of sodium in it by gentle ignition in dry hydrochloric acid as described by E. F. Smith and Philip Maas.¹

0.3620 gram of the dry salt gave 0.2044 gram NaCl.

0.1148 gram of the salt gave 0.0648 gram NaCl.

| Calculated for Na_2MoO_4 . | Found. | |
|--|--------|--------|
| | I. | II. |
| NaCl | 56.70 | 56.46 |
| | | 56.44. |

For reduction 4.3405 grams of this sodium molybdate, dried at 250° , were dissolved in 200 cc. of water. Ten cc. of the solution, therefore, contained 0.1517 gram of molybdic anhydride.

The permanganate solution used was standardized by means of ammonium oxalate and of ferrous ammonium sulphate.

0.8923 gram of the ferrous ammonium sulphate required 17.88 cc. of the solution.

0.2077 gram of the ammonium oxalate required 22.93 cc. of the solution.

These results give respectively 0.007129 and 0.007144 as the iron equivalent of the solution, and one cc. of the solution contains 0.00102 gram of available oxygen.

For reduction ten cc. of the solution of sodium molybdate referred to above were diluted with 140 cc. of water and fifty cc. of dilute sulphuric acid (1 : 5 by vol.), and the solution was passed through the "reductor"² and followed by 100 cc. of dilute sulphuric acid (1 : 100) for washing. The solution was then titrated in the flask. In all the experiments a correction was made for the amount of potassium permanganate required in blank experiments with the same quantities of dilute sulphuric acid. The corrected values are given throughout this paper.

In the first experiments amounts of potassium permanganate were required which corresponded to from 15.90 to 16.35 per cent. of oxygen as compared with the amount of molybdic anhydride present. If reduced to the form corresponding to the oxide Mo_2O_3 , 16.67 per cent. of oxygen should be required, while for the form Mo_2O_5 , but 15.74 per cent. is required. The results were not concordant and a little study of the matter led to the discovery that the reduced solution is very easily reoxidized by

¹ This JOURNAL, 15, 398.

² *J. Anal. Chem.*, 3, 123.

exposure to the air or by oxygen contained in water used for dilution. We have since found that Werncke states this fact very clearly in his paper,¹ but his statement seems to have been overlooked by recent workers and curiously enough Blair states almost exactly the contrary.²

The following illustrations of the ease with which the solution is oxidized may be given. A solution reduced as usual and which would have required at least sixteen per cent. of oxygen for its oxidation was poured into a beaker and back into the flask several times and then required only 14.89 per cent. of oxygen. A second solution reduced and then poured back and forth six times required only 13.74 per cent. of oxygen.

As it is evident from these experiments that the reduced solution must be titrated with very little exposure to the air, the reduction was next effected as follows: ten cc. of the sodium molybdate solution were diluted with 140 cc. of water and fifty cc. of dilute sulphuric acid. In the flask which was to receive the solution were placed two grams of acid sodium carbonate and five cc. of dilute sulphuric acid, thus expelling the air almost completely. A small amount of very dilute sulphuric acid was passed through the reductor first, then the molybdate solution as described and then 100 cc. of water containing five cc. of dilute sulphuric acid for washing. During all, care was taken to keep the reductor full and allow no air to pass through it. The reduced solution was titrated immediately *in the reductor flask*. Two solutions reduced in this way required respectively 24.8 cc. and 24.83 cc. of the permanganate solution, or 16.74 per cent. and 16.76 per cent. of oxygen.

The use of acid sodium carbonate for ordinary work would be somewhat troublesome and we next tried the effect of expelling most of the air from the reductor flask by passing through the reductor sixty cc. of dilute sulphuric acid (1 : 30) and following this with the solution to be reduced and the acid wash-water, taking care throughout that no air entered through the reductor tube. Ten cc. of the solution of sodium molybdate diluted with 140 cc. of water and fifty cc. of diluted sulphuric acid (1 : 5),

¹ *Ztschr. anal. Chem.*, 14, 7.

² "Chemical Analysis of Iron," p. 89.

required, when reduced in this way, 24.81 cc. of the permanganate solution, or 16.74 per cent. of oxygen.

Experiments were next tried with pure crystals of ordinary ammonium molybdate. This has the composition $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and should require if the molybdenum is reduced to the form corresponding to the oxide Mo_2O_3 , 13.59 per cent. of oxygen for reoxidation; 0.2037 gram of the salt required, after reduction as last described, 27.48 cc. of the permanganate solution; 0.2025 gram of the salt required 27.32 cc. These amounts correspond to 13.76 and 13.76 per cent. of oxygen.

Some molybdic anhydride was next prepared by gently igniting in a porcelain dish a comparatively pure specimen until all ammonia was expelled and the substance had changed to a pure yellow color, 0.1722 gram of this anhydride required, after reduction as last described, 27.76 cc. of the permanganate solution and 0.1726 gram required, 28.23 cc. or 16.44 and 16.68 per cent. of oxygen.

These experiments prove conclusively that if the reduction is properly executed the molybdenum is reduced to the form corresponding to the oxide Mo_2O_3 . The conditions are that the solution should be preceded by some dilute sulphuric acid so that most of the air in the reductor flask may be expelled before the reduced solution enters it, that the sufficiently dilute solution shall pass the reductor slowly¹ and be followed by the acid wash-water without allowing air to enter the reductor at the top, and that the reduced solution shall be titrated at once and *without further dilution*. The reduced solution should be of a pure green color and not olive-green.

After establishing the ratio between molybdic anhydride and iron for the permanganate solution there still remain two questions before we can consider the ratio between the iron and phosphorus as settled.² These are, what is the ratio between molybdic anhydride and phosphorus in the yellow precipitate, and is the precipitation of the phosphorus practically complete in the case of the small amounts usually present in a steel analysis?

¹ See Doolittle and Eavenson. This JOURNAL, 16, 241.

² The paper of Prof. S. W. Johnson (this JOURNAL, 16, 462) has appeared since this was written. The presence of aluminum or manganese in its precipitate would not affect the results of the volumetric method. Iron, if present, would affect the results and that point deserves a more careful study.

The fact that there are twelve molecules of molybdic anhydride for one atom of phosphorus has been so thoroughly established by different observers that it seems scarcely necessary to discuss the matter or even to cite authorities. The experiments of Dudley and Pease¹ can not be considered as having much bearing on this question when we consider the extreme difficulty of the gravimetric determination of such minute amounts of phosphorus and the facts with regard to the reduction of the molybdenum which have been considered above.

The question as to the completeness of the precipitation is more difficult but we believe it is best studied by the precipitation of solutions containing known amounts of phosphorus under conditions practically identical with those of the steel analysis.

A solution of sodium phosphate was prepared of such strength that one cc. contained 0.000102 gram phosphorus (determined by evaporating a measured volume of the solution, igniting and weighing the sodium pyrophosphate), three cc. of this solution were placed in a flask with five grams of ferrous sulphate, free from phosphorus (equivalent to about one gram of iron), nitric acid was added, then potassium permanganate, and the precipitation of the phosphorus was effected exactly as directed by Dudley and Pease. The precipitate, after washing, was dissolved and reduced as described in the first part of our paper. In duplicate experiments 3.08 and 3.0 cc. of permanganate were required, which gives 0.34 and 0.33 mgm. of phosphorus instead of 0.31 mgm. actually present, if we use the theoretical factor which we have deduced for the relation between iron and phosphorus. Dudley's factor on the other hand would give 0.37 and 0.38 mgm.

Determinations were also made of the phosphorus in three samples of steel containing known amounts of phosphorus which were kindly furnished us by Dr. Dudley. They are the same steels to which Dr. Dudley has already referred. We give the results of our analyses calculated by the theoretical factor obtained by multiplying the iron equivalent of the permanganate solution by 0.01538, and also by the empirical factor of Dudley and Pease.

¹ This JOURNAL, 16, 229.

| | Gravity
determination,
Per cent. | Volumetric determination. | |
|------------------|--|------------------------------|--------------------------------------|
| | | By
theoretical
factor. | By factor
of Dudley
and Pease. |
| Steel No. 1..... | 0.040 | 0.040 | 0.045 |
| " " | | 0.040 | 0.045 |
| " " | | 0.039 | 0.044 |
| Steel No. 2..... | 0.053 | 0.050 | 0.056 |
| " " | | 0.052 | 0.058 |
| Steel No. 3..... | 0.032 | 0.029 | 0.032 |
| " " | | 0.034 | 0.038 |
| " " | | 0.032 | 0.036 |

It is evident that the theoretical factor gives results which agree closely with the gravimetric determinations while the results calculated by the empirical factor of Dudley and Pease are decidedly too high. The evidence that the precipitation of the phosphorus is practically complete is quite satisfactory. It will be remembered that steel No. 2 contains arsenic. Our results seem to indicate that the arsenic is not precipitated to an appreciable extent with the phosphorus.

If the theoretical factor for the ratio between the iron and phosphorous equivalents of a potassium permanganate solution shall be confirmed by other observers, as we feel confident that it will be, the volumetric determination will be placed on so firm a basis that, at least in the absence of arsenic, the results obtained by it must be considered as more reliable than those obtained by any gravimetric method now in use. This cannot be true so long as the determination depends on an empirical factor, for any empirical factor is likely to vary with the amounts of phosphorus present and would not be applicable to steels containing widely different amounts of phosphorus.

TERRE HAUTE, JUNE 15, 1894.

THE ANALYSIS OF MALT.

BY TOM CROSSMAN.

Received June 18, 1894.

IN the JOURNAL for May, 1894, there is an article on the analysis of malt by Dr. Miller. As a few of Dr. Miller's statements are totally opposed by those who have given the chemistry of malt their life study, I feel justified in bringing before your readers the methods of analysis which are in use for the valuation

of English malts in all our large breweries. The methods being based on the splendid researches of O'Sullivan, Heron, Brown, Morris, and others. I am aware that for the English infusion mashing we require better malt than when practicing the German decoction system. No doubt the methods given by Dr. Miller would give satisfaction to those brewers working on the German principle; but I make bold to assert, that a malt tested by the methods given in the article referred to, would not give information to the brewer which would be of any great practical guidance to him.

Dr. Miller asks, "From the standpoint of the brewer, the largest consumer of malt, what are the most important points to be ascertained by the analysis of a malt?" He then gives them as follows:

1. Moisture.
2. Extract.
3. Diastatic power.
4. Acidity.

I may add that the above factors *do not* tell the brewer much; but when taken in conjunction with the following, the results give him information of the greatest possible value.

5. Ready-formed sugars, soluble in cold water.
6. The percentage of uncoagulable albuminoids, soluble in cold water.
7. The quantity of free maltose, malto-dextrins, and free dextrin, when the malt is mashed under standard conditions.
8. The amount of unmodified starch or steeliness.

With reference to No. 1, nothing need be said as far as the method is concerned; but no practical brewer would ever dream of using malt containing five per cent. of moisture. Malt having three per cent. is generally looked upon with suspicion if required for a stock ale. One per cent. is normal to a good well-cured, and properly stored article.

The determination of moisture does not in all cases give us the information whether the malt has been properly dried or not originally, since it might have gained the water during careless storage. No brewer of my acquaintance thinks of judging the price of malt by the amount of water it contains, since he

knows fully well that the increase in moisture means increased deterioration.

2. The extract is usually determined by English chemists by what is known as Heron's method.¹ It consists of mashing fifty grams of ground malt with 400 cc. of water at 68° C., and keeping the temperature of the mash at 65°–66° C. for one hour. Afterwards the mash is cooled to 15.5° C. and made up to 515 cc. (500 cc. water, 15 cc. for space occupied by grains). The gravity is taken and the extract calculated therefrom. The wort is reserved for the further analysis, 7.

Heron's method is one which has given great satisfaction, since it is possible to analyse the starch products and compare them with other malts, giving information which is very much appreciated by practical brewers. The method is, by far, preferable to that following the conversion with iodine.

As opposed to Dr. Miller's statement I find that the majority of ale brewers are more guided, when purchasing malt, by the *quality* of the extract, as determined by the tests I am enumerating, than by the *quantity*.

3. The diastatic capacity is best determined by Lintner's method, which gives us the amount of curing the malt has been subjected to. It must not be forgotten, however, that two malts, each having the same diastatic power, will not behave the same, even if mashed under identical circumstances, unless the starch in each is in the same state of friability or freeness. Since, if the one malt is hard and vitreous and the other is free, the diastase will have more "work" to perform in the former than in the latter; therefore, the relative amounts of free maltose and malto-dextrin will be quite different. This is a point overlooked by several, they thinking if malts contain a given quantity of diastase, all the starch conversions will be the same providing the temperatures are similar. This is not so. The estimation of the diastatic power is not of much use unless we know the condition of the starch as determined by 7 and 8.

4. The acidity needs no comment.

5. The percentage of ready-formed sugars convey to the brewer more information as to the quality of the malt than is generally

¹ The Polariscopes and Its Application to Brewing, (*J. Soc. Chem. Ind.*, 7, 259–276).

supposed. If the amount is low it is evident that the barley has been insufficiently germinated. If the quantity is high (*i. e.* over seventeen per cent. calculated on the malt) brewers agree that the beer produced from such a malt will not be sound; it also goes to prove that the malt has been forced or too quickly grown on the floors at high temperatures.

6. The amount of uncoagulable albuminoids and the amount of ready-formed sugars seem to bear a relation to each other. Moritz¹ has published some very interesting experiments which go to prove that under conditions specially favoring the attack and transformation of starch into sugars, there is a similar specially active attack upon the original albuminoids, and an abundant transformation of them into soluble forms. He also publishes a number of analyses of malts, and in each case he gives the factor obtained by dividing the soluble albuminoids into ready-formed sugars. It is a most noticeable fact that this factor is either 6.3, or a figure closely approximating it. There is sufficient proof here to convict the most skeptical, that it is absolutely impossible for a chemist to estimate the value of malt without first determining, 5 and 6.

7. By the estimation of free maltose and malto-dextrins, we get the knowledge how the starch is converted into the different sugars. It supplies to the brewer more information than it is at first possible, by non-brewers, to conceive; since it informs him how the starch behaves at fixed temperatures and conditions, he can then, to suit the class of beer he is desiring to produce, arrange his mashing heat with a certain amount of reliability.

Dr. Miller says, "It has been claimed by some that the percentage of sugars formed, and the amount of proteids dissolved, is of importance in judging the character of malt." I claim that the amount of sugars formed is very important in judging the character of malt, provided all malts are mashed under standard conditions, as is done when using Heron's method. I am aware that the increase or decrease of the percentage of the various transformation products is entirely dependent upon the manner in which malt is handled in the mash-tub, *combined with the condition of the starch and the amount of diastase*. Therefore, if the

¹Technical Brewing; a Report on the Chief Features, in the year 1893.

brewer gets information as to the amount of the various sugars a malt yields when mashed under known conditions, surely he has a sound foundation upon which he can base his ideas in guiding him in the manner which the malt should be handled in the mash tub. The amount of free maltose and malto-dextrin in a wort, determine, to a very large extent, the condition, flavor and attenuation of the resultant beer. I cannot sufficiently emphasize the great importance of these determinations to the practical man.

8. The amount of unmodified starch or steeliness.

This a test of some significance, but not generally practiced. Its advantages are that it gives us the amount of unmodified or vitreous starch. It will be as well if I state the objects of malting, so as to better illustrate the importance and advantages of this test. The principal objects of malting are: The dissolution of the cellulose forming the cells in which the starch granules are enclosed, and the consequent liberation of the starch; the breaking down of the nitrogen constituents of the corn; the production of diastase for the future service in the mash-tub. Now, when the original barley is bad, or the malting has not been carried out on proper lines, the cellulose surrounding the starch granules is not dissolved, the starch is "locked up," so to speak, and in a very refractory condition making it well nigh impossible for the diastase to convert it at ordinary temperatures. A large amount of starch is then left in the grains, which may possibly get "semi-dissolved" and partly washed out by the subsequent higher sparging heats, and not being converted makes the production of gray or hazy beer very easy. If it were only a matter of dealing with steely malt we could surmount the difficulty by the decoction system of mashing; but it is understood that when the dissolution of the cellulose forming the cells is not satisfactory we have evidence of the glutens being only partly modified, and the resultant beers will not be as brilliant as those produced by a fully modified malt. Thus, a malt gives the best results in practice when the amount of unmodified starch, as estimated below, is small, providing other conditions are favorable. The following is the method I have used the last two years and have found exceedingly useful:

| | | |
|-------------------|------------|---------------------------|
| Boiled mash | 77.0 | per cent. solid matter, |
| Mash (2)..... | 70.0 | " " " " |
| | <u>7.0</u> | " " of unmodified starch. |

COMPOSITION OF WORT MASHED UNDER STANDARD CONDITIONS.

When the amount of unmodified starch exceeds much over seven per cent. it is sufficient to regard the malt with suspicion. A remarkable thing and an undisputed fact is, that beer made from a good foreign malt is more sound and brilliant than when made from good English malt. Yet, on comparing the analysis of each, we find that the unmodified matter, ready-formed sugars and soluble albuminoids, are smaller in amount in the foreign

than in the English malt. This speaks volumes for the value of malt analysis when conducted as described above.

NOTE.—Preparation of cold water malt extract. Fifty grams of ground malt are added to 500 cc. cold distilled water, and allowed to stand four hours with frequent stirring. It is then filtered absolutely brilliant, and used as directed.

THE LABORATORY, ALBION BREWERY,
OLDHAM, ENGLAND.

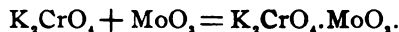
ON THE REACTION BETWEEN MOLYBDIC ACID AND POTASSIUM CHROMATE AND BICHROMATE.

BY ROBERT H. BRADBURY.

Received June 21, 1894.

MOLYBDENUM, as its position in the periodic system of the elements would indicate, offers many analogies with sulphur and more particularly with chromium. Thus, the most important acid of each is H_2RO_4 , and the most stable acid-forming oxide RO_3 . Again, sulphur and chromium have for some time been known to form a higher unstable oxide R_2O_7 , and more recently a hydrated Mo_2O_7 has been prepared and investigated.

Potassium bichromate, $K_2Cr_2O_7$, is more fully written $K_2CrO_4 \cdot CrO_3$, that is, it consists of a molecule of the neutral chromate combined with a molecule of chromic anhydride, and still higher anhydrochromates, *e. g.*, potassium trichromate, $K_2Cr_3O_{10}$ or $K_2CrO_4 \cdot 2CrO_3$, have been shown to exist. The marked likeness between molybdenum and chromium led to the supposition that it might perhaps be possible to replace the chromium in potassium bichromate by molybdenum—that is, to obtain a compound $K_2CrO_4 \cdot MoO_3$. Since the bichromate results by the direct addition of chromic anhydride to the neutral chromate, it was supposed that the hypothetical chromo-molybdate might result by simple addition of molybdic anhydride to potassium chromate, thus

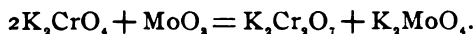


At the suggestion of Dr. Smith I have investigated this subject, and while the result is not what was expected, it is of interest as adding another to the long list of facts which show that the rôle played by a substance in a reaction depends not only on the special qualities of the substance, but also to an equal degree on the amount in which it is present. The reaction which ensues when molybdic anhydride is brought together

with chromates has been investigated : A in the case of potassium chromate, B with potassium bichromate.

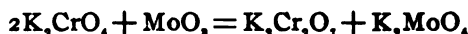
A. In determining the reaction of molybdic anhydride with neutral potassium chromate, the salt was dissolved in water and an equivalent quantity of molybdenum trioxide was added in small portions. Whether in the cold or in warm solution the molybdenum trioxide rapidly dissolves, the solution at the same time turning deep yellow-red in color. The molybdic oxide dissolves more rapidly when the process is executed in warm solution. The liquid was then slowly evaporated. At first there separated out from the solution a white mass. It was filtered, dried, and examined. It contained no chromium and was chiefly made up of unaltered molybdenum trioxide, perhaps with some potassium molybdate. The filtrate, which still retained its reddish-yellow tint, was evaporated. Further separation of the white material was constantly observed. From time to time it was again filtered off and the evaporation continued. At length a filtrate was obtained which was small in bulk and which apparently contained no more of the molybdic acid. In this, the reddish-yellow color which has already been referred to, was much deeper, corresponding with the increased concentration and showing that none of the colored material had been removed by the filtrations. This liquid was evaporated to crystallization and allowed to stand. The mass of red needles which separated was dried and recrystallized. This material was then examined. Under the microscope it did not differ from potassium bichromate, either in crystallization or in behavior toward polarized light. Analysis revealed the presence of but a trace of molybdenum and allowed no further doubt as to its nature.

The reaction between potassium chromate and molybdic anhydride therefore proceeds in the sense of the following equation :

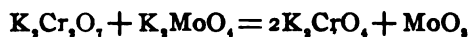


No direct addition takes place and no chromo-molybdate is produced. It follows from the fact that much unchanged molybdic anhydride separated out during evaporation and that the liquid contained a great deal of unaltered potassium chromate that the reaction is by no means quantitative. In fact the amount

of potassium bichromate formed is exceedingly small relatively to the quantities of potassium chromate and molybdic anhydride employed. Indeed we should expect from the position of molybdenum in the periodic system, from its higher atomic weight and from all the properties of its acid that the avidity of molybdic acid would be much less than that of chromic acid and therefore that the reaction



would not proceed very far before the stage of equilibrium would be reached in which the backward reaction



attains the same velocity as the principal one and in which therefore the transformation ceases.

It would be possible, probably, to increase the quantity of potassium bichromate formed by increasing the amount of molybdic anhydride until a large excess of it was present, but no experiments in this direction have been made.

B. When molybdic anhydride is introduced into a solution of potassium bichromate in the cold no change appears to occur, but no experiments beyond a rough test have been carried out in this direction. The reaction which was investigated between potassium bichromate and molybdic acid takes place only at higher temperatures. Equivalent quantities of potassium bichromate and molybdic anhydride were mixed together and heated gently in a porcelain crucible. The mixture melts rather easily to a blackish-brown liquid and at the same time an effervescence, escape of oxygen, is noticed, which becomes more energetic as the temperature is raised. When the fusion became quiet the lamp was removed. On cooling, the contents of the liquid solidified to a brown mass, which was broken up and treated with hot water. Some unchanged bichromate was removed by this procedure and the insoluble residue was thoroughly washed and dried. It is a soft, loose powder of brown color. It was then subjected to analysis.

Hydrochloric acid dissolves most of it to a green solution, giving off chlorine. A small quantity of black residue remains which is not affected by nitric acid, or by nitric acid and potassium chlorate, or by fusion with sodium carbonate and sulphur.

On this account this residue was simply dried on a weighed filter and its weight deducted from that of the substance taken.

The process of analysis may be briefly described. The material was weighed out into a beaker, addition of sufficient strong hydrochloric acid to cover it was made and the heat of a water-bath applied. After complete decomposition, the residue, invariably slight in amount, was filtered off on a weighed filter and its weight deducted from that of the substance taken. The green filtrate was largely diluted with water and hydrogen sulphide passed into it for a long period. Molybdic trisulphide (MoS_3) precipitated. It was filtered on a weighed filter and its weight determined. An aliquot portion of the precipitate was taken and ignited in a Rose crucible in a strong current of dry hydrogen to convert it into molybdenum disulphide, MoS_2 . The heat applied here must not be too high, or part of the material volatilizes yielding a black sublimate and loss of weight is the result. The molybdenum disulphide was allowed to cool in the current of gas and then weighed, and the quantity of molybdenum corresponding to the whole of the precipitate and therefore to the substance taken was found by the appropriate calculations. From the filtrate the chromium was precipitated as hydroxide by the addition of ammonia and was estimated in the usual way as sesquioxide.

The potassium in the filtrate from the chromium was weighed as usual, as chloride.

The results follow:

| | A. | B. | C. | Mean. |
|---------------------------|-------|-------|-------|-------|
| Mo..... | 43.69 | 43.56 | 43.17 | 43.45 |
| Cr | 14.71 | 14.65 | 15.00 | 14.79 |
| K | 11.08 | | 11.86 | 11.47 |
| Oxygen by difference..... | | | | 30.29 |

The formula $\text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{MoO}_3$ requires the following composition:

| | |
|----------|-------|
| Mo..... | 42.42 |
| Cr | 15.44 |
| K | 11.51 |
| O | 30.63 |

The compound in question is thus a basic molybdate of chromium and potassium.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

ACTION OF MOLYBDENUM DIOXIDE UPON SILVER SALTS.

BY EDGAR F. SMITH AND OWEN L. SHINN.

Received June 15, 1894.

It has been shown (*Ztschr. anorg. Chem.*, 1, 360) that metallic molybdenum precipitates metallic silver from ammoniacal argentic solutions, but no record seems to have been made of the fact that molybdenum dioxide behaves similarly. This, however, was observed to be the case on introducing dioxide, prepared by the reduction of trioxide in a current of hydrogen, into an aqueous argentic nitrate solution for the purpose of learning whether any metal was present in the dioxide. All of the material dissolved on the application of a gentle heat. The solution was especially rapid in the presence of a slight quantity of ammonia. The silver separated in crystalline leaflets. Attempts were made to discover whether the reaction was really quantitative. The results are as follows:

1. 0.1057 gram brown dioxide, prepared by the reduction of ordinary molybdic acid in an atmosphere of hydrogen, precipitated from a slightly ammoniacal argentic nitrate solution 0.1755 gram metallic silver.

2. 0.1772 gram of dioxide precipitated 0.2915 gram of metallic silver. The latter was washed with dilute ammonia and with water.

Thinking that possibly the dioxide as prepared for the preceding precipitations did not really represent that oxide, but a mixture of oxides, recourse was had to a method first suggested by Manro and Pauebianco (*Gazz. chim. ital.*, 11, 501). Muthmann (*Annalen der Chem.*, 238, 116) employed this method with success. It is, briefly, the fusion of eight grams of dehydrated ammonium molybdate, seven grams of molybdic acid, fourteen grams of ignited potassium carbonate and seven grams of boric acid in a capacious and well-covered platinum crucible. The mixture should be held for several hours in a liquid condition. On cooling, a brittle mass results; it contains crystals of the dioxide. It can be readily detached from the crucible. The

570 ACTION OF MOLYBDENUM DIOXIDE UPON SILVER SALTS.

brown oxide was purified by washing with ammonia water and then with pure water. The two reductions made with this oxide resulted as follows :

3. 0.3698 gram of oxide precipitated 0.6250 gram of silver.
4. 0.5287 gram of oxide threw out 0.8799 gram of silver.

In both cases ammonia, sufficient to precipitate silver oxide and again dissolve it, was added to the argentic solutions. The precipitated silver was also washed with ammonia water and finally with pure water.

If the ratio between the dioxide and the silver be deduced from the figures given in the preceding experiments it will be found to approach



and then the calculated or theoretical quantity of silver required for the dioxide used in the various experiments would be

| | Calculated Ag. | Found Ag. |
|--------|----------------|--------------|
| 1..... | 0.1783 gram. | 0.1752 gram. |
| 2..... | 0.2990 " | 0.2915 " |
| 3..... | 0.6240 " | 0.6250 " |
| 4..... | 0.8765 " | 0.8799 " |

The results in 3 and 4 agree more nearly with the theoretical requirements than those in 1 and 2, doubtless because the oxide used in those experiments was a true molybdenum dioxide. Their variation from the theory may be ascribed in 3 to slight solubility of the precipitated metal in ammonia, and in 4 to minute traces of molybdic acid in the silver.

Additional trials were made to arrive at more concordant results, but success was not achieved, although in every instance the resulting silver approximated the ratio previously established. This reaction, while apparently useless for quantitative purposes, is yet of interest as it shows that the precipitation of metallic silver is not confined to metallic molybdenum, but that it even extends to the dioxide and perhaps to other mixed oxides of which the dioxide may be a part.

It is of interest to note in connection with the conduct of molybdenum dioxide as outlined in the preceding paragraphs, the further analogy established between it and the dioxides of other metals of Group VI. Thus, tungsten dioxide reduces not only copper and mercuric salts, but also precipitates metallic

silver from ammoniacal silver solutions, and uranium dioxide, prepared by reduction of the oxalate in a current of hydrogen, dissolves in silver nitrate with the separation of metallic silver. Molybdenum dioxide showed no reducing action upon copper and mercuric salt solutions.

Among the non-metals of Group VI we observe in the deportment of sulphites towards silver nitrate, in the breaking down of silver sulphite into metallic silver on the application of a gentle heat, a behavior analogous to that exhibited by molybdenum dioxide, and which we may consider as an additional contribution to the many already well-established analogies, existing among the derivatives of the elements constituting Group VI of the Periodic System.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

NEW BOOKS.

PRACTICAL INSTRUCTIONS IN QUANTITATIVE ASSAYING WITH THE BLOW-PIPE. CONTAINING ALSO READILY APPLIED QUALITATIVE BLOWPIPE TESTS. BY E. L. FLETCHER. pp. 142. 14 Illustrations. Price, 12 mo. cloth, \$1.25; morocco, \$1.50. New York: John Wiley and Sons. 1894.

The manual of blowpipe analysis contains 142 pages with numerous cuts showing apparatus. It is well printed on serviceable paper and is of convenient size to be carried in the pocket.

Chapter I consists of descriptions of apparatus and general directions for their use, also in some cases the price of special appliances.

Chapter II is devoted to reagents, those commonly used in assaying, etc.

Chapter III contains descriptions of the various colored coats and flame tests given by the volatile elements.

Chapter IV describes the colored beads produced by all of the common and many of the rare elements when dissolved in borax or salt of phosphorus, both with the oxidizing and reducing flames.

Chapter V gives the method of reducing oxides on charcoal with soda.

Chapter VI. This chapter is the best in the book; here the ordinary qualitative blowpipe tests are distinctly and succinctly described.

Chapter VII, Quantitative assaying, describes in considerable detail the operations of sampling and of making quantitative blowpipe assays for silver, gold, lead, copper, tin, mercury, nickel, cobalt, and bismuth.

The appendix contains tables of hardness, atomic weights, etc.

A defect in the book is that the weights of ore are given in grains while the divisions, on the scale, used for measuring the size and hence determining the weight of the buttons, reads milligrams, thus making calculations necessary which would be simplified by the use of the assay ton system.

In regard to the accuracy of the results obtainable by the methods described, granting that the button can be measured accurately to a cross-line of the scale, the differences are so great as to render the method nearly useless for ordinary gold ores. Cross-line No. 1=18 cents a ton in gold, No 2=\$1.40 a ton, No. 3=\$4.80 a ton, No. 4=\$11.60 and so on.

The book may prove useful to prospectors, skilled in the use of the blowpipe, who have the good fortune to discover rich veins.

E. H. M.

MINERAL RESOURCES OF THE UNITED STATES CALENDAR YEAR 1893. BY DAVID T. DAY, 8 vo. pp. v, 810, Washington, D. C.: Government Printing Office. Price 50 Cents.

This annual volume so well known to those interested in the mining industry carries forward the statistics to Dec. 31, 1893, and gives much descriptive matter to a later date. The following statements are of especial interest to chemists:

Aluminum.—"The total production of aluminum reached 333,629 pounds. * * It can be said that nearly all the steel makers use a small proportion of aluminum with the result of less waste in castings. For example, the amount of waste in crop ends on steel rails is lessened profitably. Ingot aluminum also goes to manufacturers of aluminum cooking utensils and this industry is extending satisfactorily. The remainder of the product goes out as sheet and wire for many purposes including

numberless experimental uses, among them lithographing with aluminum plates instead of zinc or lithographic stone. Some experiments in this direction in the map department of the Geological Survey indicate that the transfers obtained on aluminum are superior to those on zinc."

Salt.—"Notwithstanding the low prices which have prevailed and which have been due to keen competition among producers, there has been a laudable endeavor on the part of a number of manufacturers to improve the quality of their product. In this, signal success has been attained, and salt of American production has been so improved by new processes, which each producer holds secret, that importations of refined salt have almost ceased to be a factor in the industry. The competition in the production of fine grades of salt has become as sharp in its way as the competition in prices. Table and dairy salts are now prepared for commerce practically chemically pure—free from gypsum, calcium chloride, and magnesium salts."

Space will not permit of further extracts from this useful volume.

E. H.

SEVENTH ANNUAL REPORT AGRICULTURAL EXPERIMENT STATION OF NEBRASKA FOR THE YEAR 1893. pp. 206. Lincoln, Nebraska: State Journal Co. 1894.

The volume includes brief statements of the work of the year by the director and the heads of the different departments, a list of books in some of the sections, the usual roster of officers and the financial statements. With these are bound nine articles which have already appeared as station bulletins and the title page of one other.

Chemists will be most interested in the two articles on the culture of the sugar-beet by Prof. Nicholson and his assistants, and in the article on the influence of changes of food and temperature on the quantity and quality of the milk of dairy cows.

The work on the sugar-beet is planned to cover the subject thoroughly, including culture, yields, richness of the beet, value of rejected portions, study of physiological problems, effect of fertilization, cost of production, seed production, and injury from insects.

Since Nebraska has become the second beet-sugar producing state in the union, parties interested in the subject naturally look to the bulletins of the Nebraska station for reliable information on the subject. They will find much important matter in this report. The work has been carried out on a larger scale than is usual in experiment station work. Under the head of fertilizers for beets it is stated that the use of "guano" seemed to be injurious to the beet. It is to be regretted that the actual composition of this "guano" is not given, as the "guano" now sold is often very different in origin and composition from the guano of standard reference books.

All the articles are fully illustrated by cuts, plates, and charts which add very materially to the interest and value of the volume.

H. A. HUSTON.

ELECTRO-CHEMICAL ANALYSIS. BY EDGAR F. SMITH. pp. 139, 27 illustrations. 2d Edition. Price \$1.25. Philadelphia: P. Blakiston, Son & Co. 1894.

It is to Germany that we are accustomed to look for the scientific thoroughness which characterizes this little volume. Prof. Smith has long been known as an indefatigable worker in the field of electrolysis, and is a frequent and regular contributor to its literature. In this manual he presents, in clear and precise language, all that has stood the test of experience, and he deserves praise for avoiding to give undue prominence to his own methods. The very interesting chapter which he devotes to an historical sketch of the subject will doubtless serve to dispel erroneous notions that are entertained by many chemists regarding the authorship of certain methods.

In this new edition the character of the original work is preserved, but the additions show that the author has not allowed any recent publications of importance to escape his attention. Amongst others we note references to the interesting work of the Munich Polytechnic School, the valuable experiences of Elbs and of Oettel, and especially the excellent work that has been done in the laboratory of the University of Pennsylvania since the appearance of the first edition.

There is, no doubt, that we have here the most accurate, as well as the most complete work that has been written on electro-chemical analysis.

H. F. KELLER.

THE ALCHEMICAL ESSENCE AND THE CHEMICAL ELEMENT. AN EPISODE IN THE QUEST OF THE UNCHANGING. BY M. M. PATTISON MUIR. pp. 94. London: Longmans, Green & Co. 1894. Price \$1.50.

This essay is a study "of the endeavors that men have made to give definiteness to the conception of unity of material phenomena" in the domain of chemistry. The discoveries and theories of the alchemists are summed up with no lack of appreciation, and the author proposes to judge the value of alchemical conceptions by finding "what results flowed from applying these conceptions to the study of nature." What, secondly, has chemistry accomplished by "examining material changes accurately and critically?"

The answers are given with dignity and fairness. The book is interesting; it seems intended for, and is adapted to the use of intelligent people who are not chemists, and contains home thrusts at some who are called "Modern Alchemists."

NINTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

CIRCULAR OF ANNOUNCEMENTS.

THE Ninth General Meeting of the AMERICAN CHEMICAL SOCIETY will be held in Brooklyn, N. Y., on Wednesday and Thursday, August 15th and 16th, 1894. The first session will be held at 10 A. M., August 15th, in room 42 of the Polytechnic Institute, No. 99 Livingston street. After the session, at 1.30 P. M., it is expected that a steamer will leave one of the wharves of the East river taking the chemists to the New York side where a lunch will be served at the mineral water establishment of Mr. Carl H. Schultz. After lunch there will be an opportunity to inspect the manufactory, and then the steamer will proceed to the U. S. Artillery School at Willet's Point, stopping at intermediate places of interest, and returning to Brooklyn in the evening.

The morning session on Thursday will begin at 9 A. M., and later in the day visits will be made to manufactories in the vicinity, returning in time for the address of Vice-President Norton before Section C of A. A. A. S., at 4:30 P. M.

Invitations have been received to visit various chemical establishments and places of scientific interest, and the local committee will arrange for such visits at convenient times during the two days appointed for the meeting of the American Chemical Society and the remaining days of the week, as the chemists who remain to participate in the meetings of the A. A. A. S. will undoubtedly be glad to avail themselves of such opportunities. The local committee of arrangements for the meetings of the A. A. A. S., and the other bodies which will be in session in Brooklyn at or near the same date, have secured for all of these organizations railroad rates of one and one-third fare for the round trip to Brooklyn or New York and return, under the following conditions:

(1) Each person, in order to secure said rates, must purchase a first-class ticket to Brooklyn or New York and pay full fare therefor, obtaining from the ticket agent a certificate to that effect upon a regular printed form. Such certificates will be available from August 10th—five days before the opening of the meeting. In case the agent at the starting point is not supplied with certificates or cannot give through tickets, the regular fare must be paid to the nearest station where such certificates can be obtained.

(2) These certificates must be deposited by holders, on their arrival at Brooklyn, with the Local Secretary, Prof. Geo. W. Plympton, who will return them when desired for the return trip.

(3) Before presenting these certificates at the ticket office in Brooklyn for obtaining return tickets they must be filled in on the back by the Local Secretary and also countersigned by the Special Agent of the Trunk Line Association. The Special Agent will be in attendance August 16th, 18th, 20th, and 24th.

(4) Certificates and return tickets are not transferable and the certificates will not be received by the Ticket Agents in Brooklyn after August 31st.

ALBERT C. HALE,

Gen. Sec'y of the American Chemical Society.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

AN ATTEMPT TO PREPARE MOLYBDENUM
HEXACHLORIDE.

BY EDGAR F. SMITH AND HENRY C. BURR.

Received June 15, 1894.

IT is well known that Teclu¹ obtained the hexachloride of tungsten by acting upon the trioxide of the metal with phosphorus pentachloride. The treatment of molybdenum trioxide in the same manner gave in one instance the compound $\text{MoCl}_5 \cdot \text{POCl}_3$ and in another, $\text{MoCl}_5 \cdot \text{PCl}_5$. In both of these derivatives the pentachloride of the metal is present. It would, therefore, seem that the metal is incapable of carrying the sixth chlorine atom. Reuter² heated both the trioxide of tungsten and that of molybdenum with silicon tetrachloride; his products, however, were not hexachlorides. Passing by his observations it was thought that if a partially chlorinated molybdic acid were exposed to chlorinating agents the residual oxygen might be removed and that then perhaps the hexachloride would be present in the reaction product. To this end molybdenyl chloride, MoO_2Cl_2 , was mixed with an equivalent quantity of phosphorus pentachloride and heated in a sealed tube in the presence of chlorine to a temperature of about 170°C . On cooling, it was found that the tube contained a mass of greenish-black crystals, which when carefully freed from adherent phosphorus oxychloride by distillation in an atmosphere of chlorine gave a product that on analysis yielded figures approximating the pentachloride more closely than the hexachloride.

Silicon tetrachloride was substituted for the phosphorus pentachloride and the experiment repeated. The resulting crystalline

¹ *Ann. Chem.*, (Liebig's), 187, 255.

² Dissertation, Tübingen, 1893.

product was quickly removed to a boat and carefully distilled in an atmosphere of carbon dioxide. Brown vapors were expelled from the boat, which finally contained nothing but white silica. The brown vapors quickly condensed in the colder portion of the tube, and upon analysis gave results varying between those required by the tetrachloride and pentachloride.

The conclusion to be drawn from these experiments then is that notwithstanding the molybdenum atom has already been partially chlorinated, and apparently is in a suitable condition to pass into the hexachloride, it yet does not do so, and we can hence only say that the molybdenum is either not sexivalent towards chlorine, or that at the elevated temperature at which these reactions took place, the hexachloride, if formed, cannot exist, but is dissociated into lower chlorinated derivatives.

On heating pure, finely divided molybdenum, intimately mixed with sugar-carbon, in an atmosphere of chlorine the invariable product was the pentachloride.

The temperature doubtless exerts a great influence in these reactions.

It has been observed in this laboratory that when metallic molybdenum acts upon an aqueous solution of ferric chloride rapid reduction of the ferric salt ensues with accompanying solution of the molybdenum. From a careful determination of the amount of iron thus reduced, the molybdenum evidently dissolves as a hexad, and it may be that if such solutions were allowed to evaporate slowly in desiccators, the hexachloride or some double salt, formed from it and ferrous chloride, might be found. Search will be made in this direction.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

THE ACTION OF HYDROCHLORIC ACID GAS UPON SODIUM VANADATE.

BY EDGAR F. SMITH AND JOS. G. HIBBS.

Received June 18, 1894.

THE reaction of Debray¹—the volatilization of molybdic acid by means of hydrochloric acid gas,—has suggested a number of experiments which of late have been tried in various

¹ *Compt. rend.*, 46, 1098.

directions in this laboratory. Among others we have exposed sodium pyrovanadate to the influence of the gas at temperatures ranging from the ordinary to about 440°C ., and have found that it is possible in this manner to eliminate the vanadic acid from its salts.

In several experiments we used a preparation from Merck, marked "sodium vanadate." It was not white in color, but showed here and there spots that were yellow to reddish-brown. Weighed portions of this salt, after complete drying, were exposed in boats, to the action of pure hydrochloric acid gas. As soon as the boats were introduced into the gas the salt, *in the cold*, acquired a red-brown color. On the application of a gentle heat, vapors of similar color appeared over the boat and condensed in the colder, anterior portion of the combustion tube to a reddish-brown, semi-transparent, oily liquid, which was taken up by water with a brown color. In the boat remained sodium chloride, containing here and there minute black spots. On dissolving the salt, the black insoluble material was carefully examined and proved to be traces of vanadic oxide. They were undoubtedly present in the original salt and were the real cause of the reddish color noted in it. That they were not volatilized may be due possibly to the fact that they had previously undergone strong ignition, and were hence less volatile, although it was observed that by continued heating of the salt, while yet exposed to hydrochloric acid vapor, they gradually grew less in quantity. The results obtained in the four experiments, which follow, while they do not agree with the theoretical requirements yet show that the source of error was constant.

1. 0.0795 gram sodium vanadate gave 0.0546 gram sodium chloride, whereas if the salt analyzed had been pure sodium pyrovanadate it should have given 0.0606 gram sodium chloride.

2. 0.0786 gram sodium vanadate gave 0.0535 gram sodium chloride, instead of 0.0599 gram.

3. 0.1006 gram vanadate gave 0.0683 gram sodium chloride, instead of 0.0767 gram.

4. 0.1322 gram vanadate gave 0.0916 gram sodium chloride, while theory required 0.1007 gram.

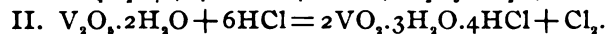
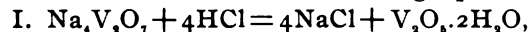
Taking the purest vanadic acid that we could find, pyrovana-

date of sodium was prepared and obtained pure after several recrystallizations. The anhydrous material was exposed to hydrochloric acid gas as before with results that indicate a quantitative separation of the acid.

1. 0.1240 gram sodium pyrovanadate heated to 440° in hydrochloric acid gas gave 0.0935 gram of salt instead of 0.0945 gram.

2. 0.2197 gram sodium pyrovanadate gave 0.1669 gram sodium chloride, while theory requires 0.1672 gram.

The sodium chloride from these last two experiments was perfectly white in color, soluble without residue in water, and on examination showed no evidence of the presence of vanadium. The volatile product had the appearance of the compound $2\text{VO}_3 \cdot 3\text{H}_2\text{O} \cdot 4\text{HCl}$ obtained by Berzelius when acting on vanadic acid with concentrated hydrochloric acid. If such be really the case we may suppose that in our reaction changes occurred similar to those indicated in the following equations:



It will, however, be necessary to subject this volatile product to careful analysis before making a positive assertion in regard to its composition.

It is our intention to pursue this study further with the view of ascertaining whether by means of this reaction it will be possible to separate vanadic acid from certain of its associates from which it is now removed with difficulty. From the ease with which the transposition occurs we may hope that the atomic mass of vanadium may be determined after the same fashion as was done in the case of molybdenum.¹

UNIVERSITY OF PENNSYLVANIA.

June, 1894.

ON SOME OF THE ARSENIC TESTS OF THE U. S. PHARMACOPOEIA (1890).²

BY CHARLES O. CURTMAN.

Received June 15, 1894.

NOTE.—In applying Bettendorf's test for arsenic, the Pharmacopoeia directs that to a small quantity of the liquid to be tested, which should contain much hydrochloric acid, or should be a solution of the substance

¹ *Ztschr. anorg. Chem.*, 5, 280.

² Report of the Pharmacopoeial Research Committee B.

to be tested in pure, concentrated hydrochloric acid, there should be added an equal volume of a saturated solution of freshly prepared stannous chloride in pure, concentrated hydrochloric acid, *together with a small piece of pure tin-foil*. The presence of arsenic is revealed by the production of a brown color or brown precipitate, the appearance of which is hastened by a gentle heat. By an oversight, the direction to add the tin-foil was inserted or left standing in the tests for arsenic in bismuth or antimony salts, in which it leads to false conclusion, as the following paper will show. (Dr. Chas. Rice, Chairman U. S. P. Revision.)

A NUMBER of experiments have been made for the purpose of ascertaining the conditions most favorable to the result of the test for arsenic by stannous chloride (Bettendorf's test and its modifications).

The inquiry was directed to the following points:

1. The limit of sensitiveness of the test in its various modifications.
2. The best proportion of reagent to specimen.
3. The influence of the use of metallic tin together with the stannous chloride.
4. The influence of the presence of other substances in the specimen tested.

I. LIMIT OF SENSITIVENESS.

The following reagents were used:

- a. The solution directed for Bettendorf's test by the U. S. P., consisting of a saturated solution of pure stannous chloride in pure, concentrated hydrochloric acid. The specific gravity of this solution was 1.407.
- b. Metallic tin, perfectly pure, in thin cylinders, from which shavings of about 0.1 gram were taken as needed.
- c. Stannous chloride solution prepared according to the German "Arzneibuch," by saturating a mixture of five parts of crystals of stannous chloride and one part of hydrochloric acid with dry hydrochloric acid gas. The specific gravity = 1.912.

All of the materials used were previously tested for absence of arsenic by Gutzeit's test, so as to exclude any fallacies arising from the introduction of even small traces of arsenic by the reagent, which might cumulate with those in the specimen.

It was easy enough to procure pure metallic tin, but impossible to obtain, from local dealers, hydrochloric acid sufficiently

free from arsenic to stand Gutzeit's test for one hour. So that I had to distill from purified sulphuric acid and pure sodium chloride the hydrochloric acid required for the preparation of the reagents.

A number of specimens of arsenic solution were made, containing free trioxide, sodium metarsenite and sodium arsenate in such proportion that each set corresponded exactly to an equal amount of As. They were:

Arsenic trioxide ($\text{As}_2\text{O}_3 = 197.68$), of which 1.31962 grams contain one gram of As.

Sodium metarsenite, ($\text{NaAsO}_2 = 129.82$), of which 1.7332 grams contain one gram of As.

Sodium arsenate, U. S. P. ($\text{Na}_2\text{HAsO}_4 + 7\text{H}_2\text{O} = 311.46$), of which 4.51834 grams contain one gram of As.

The solutions used for experiment contained from 0.5 gram to 0.01 gram of As. Of these, one cc. was used for each trial and the amount of reagent mixed with this varied from one cc. to three cc., so as to correspond with the limits prescribed in the pharmacopoeial tests. When metallic tin was added to the reagent, one cc. each of the specimen and the stannous chloride solution was used. In some cases of doubt a ten-fold quantity (10 : 30 cc. etc.) was used to obtain sufficient material for colorimetric comparison.

A uniform application of heat was effected whenever needed by imbedding the series of test-tubes under observation, to an equal depth, in a sand-bath heated to about 80° C.

Whenever comparisons of color became necessary to decide whether a deeper color had been produced than that of the unaffected reagent (as was especially necessary with the yellowish solution of the German pharmacopoeia), or whether a greater or less intensity of color characterized the reaction, narrow graduated cylinders of ten cc. capacity, were used in a dark box with light reflected from beneath, or occasionally for still greater accuracy, a pair of Hehner's colorimeter cylinders of 100 cc. capacity, also placed for observation into a dark box, admitting from beneath light reflected upward by a plate of milk-glass placed at an angle of 45°. With the aid of these appliances the following results were obtained:

a. With the U. S. P. solution of stannous chloride of sp. gr. 1.467, one cc. of each of the three specimens, containing 0.5 mgm. of As, was mixed in the different proportions stated below, and kept at ordinary temperature for one hour.

With one cc. of reagent a sharp reaction had taken place at the end of the hour. With two cc. of reagent the reaction was obtained earlier and was more intense at the end of one hour. With three cc. of the reagent the reaction was still more speedy, and at the end of the hour more intense.

No difference could be noticed either in time or in intensity between arsenic in the state of trioxide or pentoxide.

When the test-tubes were arranged exactly as before, but placed in hot sand, the time was somewhat shortened, and a slight increase of intensity noticed in all of the specimens.

b. When one cc. of the U. S. P. solution was used with one cc. of solutions containing 0.5 mgm. of As, and a small piece of metallic tin added and heat applied, the reaction was almost instantaneous, and in three minutes a very sharp, unmistakable coloration appeared which continued to increase in intensity for about ten or fifteen minutes, but was not notably darker at the end of the hour. No difference appeared in the different solutions containing arsenite and arsenate.

c. When from one to three cc. of the stannous chloride of the German pharmacopeia was used with one cc. of the solutions containing 0.5 mgm. of As, there was a slight darkening of the color in a few minutes, which continued to increase to the end of the hour. No difference was perceivable between the arsenous and the arsenic preparations. At fifteen minutes the specimens treated by the U. S. P. solution and metallic tin showed a much greater intensity of color, but toward the end of the hour there was but little difference perceptible between the color of the specimens treated with three cc. of the German reagent without heat, and that treated with one cc. of the U. S. P. reagent, metallic tin, and heat. The specimens containing less than 2.5 cc. of reagent showed a less intense color.

These experiments were repeated with the three solutions containing 0.05 mgm. of As. in one cc. and resulted as follows:

a. With the U. S. P. solution of stannous chloride: One cc.

gave no reaction during forty-five minutes, then gradual coloration began. If heat be applied the reaction begins in eighteen minutes and at the end of one hour is slightly more intense than when treated without heat. 1.5 cc. of reagent: reaction slightly more rapid and intense than with one cc. 2.0 cc. of reagent: still more rapid and intense, both with and without heating. 2.5 cc. of SnCl_2 : reaction begins in fifteen minutes at air temperature in less than five minutes when heated. 3.0 cc. of SnCl_2 : reaction slightly less intense than with 2.5 cc., both hot and cold. 3.5 cc. of reagent: a still further slight decrease in intensity. No difference could be observed in the reaction of As_2O_3 and As_2O_5 ; the sodium metarsenite appeared to be very slightly more colored than As_2O_3 .

b. With one cc. of the U. S. P. solution and a small piece of metallic tin, at a temperature of about 80°C ., one cc. of the solutions containing 0.05 mgm. of As, began showing a brownish color at thirteen minutes. At thirty-five minutes the reaction was quite sharp and continued to grow slowly in intensity to the end of the hour. No difference was perceptible between As_2O_3 and As_2O_5 .

Three cc. of the solution of the "Arzneibuch" mixed with one cc. of the solutions containing 0.05 mgm. of As, began showing a feeble reaction at thirty-five minutes, and at the end of the hour showed a plain reaction as compared with the unchanged reagent, but did not equal in intensity, the reaction produced by the addition of metallic tin.

On repeating the experiments with solutions containing 0.03 mgm. of As in one cc., a feeble reaction resulted from the use of stannous chloride and metallic tin at the end of an hour, but even after standing over night the other methods gave such a faint reaction that it required close inspection in the colorimeter to perceive the change. A solution containing 0.02 mgm. of arsenic failed to show any reaction. So I think that for practical purposes the utmost limit of reaction is reached at 0.03 mgm. of As in one cc. and that the method employing metallic tin and heat is to be preferred where the presence of antimony or bismuth does not forbid its use. Even the addition of pure, concentrated sulphuric acid, which was recommended when the

test was first introduced, has not yielded to me any substantial advantage in detecting the presence of arsenic in greater dilutions.

II. THE BEST PROPORTION OF REAGENT TO SPECIMEN.

In the foregoing experiments and a number of others conducted for that purpose it was observed that both with the U. S. P. solution (without the use of metallic tin) and with that of the German pharmacopoeia, the greatest intensity of color obtained after an hour's reaction occurred when one cc. of the arsenical solution was mixed with 2.5 cc. of the reagent. Between three cc. and two cc. of the German solution hardly any difference could be found. But with the pale U. S. P. solution a very slight difference appeared in favor of two cc. as against three cc. Heat did not appear to affect the proportion needed.

When metallic tin was added it seemed to be best to use equal volumes of specimen and reagent, although the variable amount of dark coating of reduced arsenic adhering to the tin prevented an accurate comparison.

III. INFLUENCE OF THE USE OF METALLIC TIN TOGETHER WITH STANNOUS CHLORIDE.

When metallic tin is heated with pure concentrated hydrochloric acid, a copious evolution of hydrogen results. When heated with the saturated solution of stannous chloride in hydrochloric acid, the evolution of hydrogen is but scant. When arsenic is mixed with the solution, the evolution of gas is perceptible but very feeble. Very little arsine appears to be evolved, for a paper cap with a drop of acidulated silver nitrate does not show any evidence of the reduction by AsH_3 , for over fifteen minutes, and even at the end of an hour but a very faint arsenic reaction is seen.

To ascertain whether any of the arsine formed would react with the stannous chloride and thus hasten the reduction of As, I arranged a small apparatus in which a copious current of arsine, mixed with hydrogen, was generated and after passing through a bottle filled with dry cotton, was permitted to bubble through stannous chloride solution of the U. S. P. After more than an hour's time not a trace of coloration could be detected. So that after arsine has once been formed it is not again decomposed by

stannous chloride. Hence the prompt action of metallic tin must depend upon the *nascent* hydrogen, which aids the stannous chloride in reducing the trioxide and pentoxide.

But, however satisfactory the action of metallic tin in accelerating and intensifying the reduction of arsenic, it *cannot* be employed to detect arsenic in preparations of *bismuth or antimony*. For *the metallic tin reduces both of these metals*, and precipitates them from their solution as black floccules, which aggregate into small granular lumps. There could be a distinction made between the firm floccules of Sb or Bi and the finely divided brown particles of arsenic, but it would hardly be safe to trust to this appearance for a sufficient evidence of the presence of arsenic, and the preparations of Bi and Sb *must be tested without the aid of metallic tin*.

A number of specimens of pure bismuth and antimony salts were tested with the U. S. P. and the German solution of stannous chloride in various proportions. But neither at ordinary temperature nor when heated did the least coloring occur.

IV. INFLUENCE OF THE PRESENCE OF OTHER SUBSTANCES IN THE SPECIMEN TESTED.

The preceding experiments were made with a solution of either arsenic trioxide or sodium metarsenite or arsenate in water, other substances being absent. But in testing various chemicals for traces of arsenic there are different conditions, as the arsenic forms only a very small portion of the mixture. In the U. S. P. the Bettendorf test is directed for eleven preparations. For hydrobromic, hydrochloric, phosphoric, and sulphuric acids, one cc. of the acid is to be tested by mixing with one cc. of the reagent, adding a small piece of tin-foil and heating. In case of magnesium sulphate, one gram of the dry substance is to be shaken with three cc. of the reagent; metallic tin is then to be added and an hour allowed for the appearance of the reaction; sodium phosphate, and pyrophosphate are treated in like manner, but heat applied and fifteen minutes time given.

In the case of Antimony and potassium tartrate, antimony oxide, bismuth subcarbonate, and bismuth subnitrate, it was intended to test with stannous chloride alone for an hour, but by an unfortunate misunderstanding of the transcriber, tin-foil was

directed to be added, which will reduce Sb and Bi as well as As.

To find whether any of the chemicals directed to be tested by the stannous chloride method, could influence the detection of arsenic, specimens were prepared containing the pure chemicals shown to be free from arsenic by other tests, and with these small portions of arsenic were mixed and the tests compared with those in which arsenic was present in equal amount without admixture with the chemicals.

In no case could any difference in the intensity of the test be made out, nor were the differences in the time of the occurrence of the coloration sufficiently great or regular to justify the assumption that the reaction was impeded or accelerated by the presence of other salts.

ST. LOUIS, May 27, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY. No. 8.]

THE INFLUENCE OF ALUM, ALUMINUM HYDROXIDE AND ALUMINUM PHOSPHATE, ON THE DIGESTIBILITY OF BREAD.

BY W. D. BIGELOW AND C. C. HAMILTON.

Received June 28, 1894.

THE property which alum possesses of arresting the fermentation of flour, and making it possible to prepare presentable bread from very inferior flour has long been known, and the adulteration of flour by means of alum has been extensively practiced by millers and bakers. Comparatively little attention has been given to this subject in this country, but in Europe, especially in England, the question has been constantly before the minds of the public analysts for at least a quarter of a century. Indeed, as early as 1821 a law was passed prohibiting the addition of alum or any aluminum compound to flour or bread. This law remained in force till 1861 when it was repealed by the passage of a law which made it necessary for the prosecution to prove the injurious quality of the substance added.

It is universally admitted that the presence of alum as such not only impedes digestion but also exercises an injurious effect on the digestive organs. There is one phase of the alum question, however, to which a great deal of attention has been

given, both in this country and abroad; namely, the use of alum as the acid compound of baking powders. Unlike the practice of adding alum to flour or dough, this question has been attended with a long continued and fiercely contested controversy.

Many experienced analysts who have condemned alumed bread in unmeasured terms, have testified that in their opinion, bread baked with alum baking powders exercises no injurious influence on digestion or the digestive organs.

In the famous Norfolk¹ baking powder case, it was contended by the Government that alum united with the soluble phosphates of the flour with the formation of an insoluble compound, and that the flour was thus deprived of one of its most valuable constituents.

The defense, on the other hand, claimed that the aluminum was entirely precipitated as hydroxide. It is a curious fact that shortly after the Norfolk case the manufacturers of alum baking powders began the addition of acid calcium phosphate, and the position taken by prosecution and defense in the Norfolk case were reversed in a recent case² before the English courts. In the evidence submitted by the prosecution independent experiments were cited by Dunstan, Hehner, and Claude Thompson, to prove that aluminum hydroxide dried at 100° was soluble in two-tenths per cent. hydrochloric acid. Dunstan found aluminum hydroxide dried at 100° to be soluble in the gastric juice of a dog diluted to two-tenths per cent. of its normal strength, and that this fluid diluted to the same extent dissolved aluminum hydroxide from bread baked with the powder manufactured by the defendant.

Dunstan also found that aluminum hydroxide in bread interfered with the action of diastase (hence, with ptyalin, the digestive ferment of the saliva), and with peptic and pancreatic digestion. Also, that a three-tenths per cent. solution of sodium carbonate (the strength of the alkali in the intestinal juice) would dissolve aluminum hydroxide which had been dried at 100°. He also testified that he had found an aluminum salt in the urine of a man who had eaten one to two grams of aluminum hydroxide which had been dried at 100°.

Morgan testified that he had dissolved aluminum hydroxide

¹ *Analyst*, 1879, 4, 231, and 1880, 5, 21.

² *Analyst*, 1893, 18, 152; *Chem. News*, 1893, 67, 213.

which had been dried at 100° in his own vomit and in that of hisson.

On the other hand, the defence took the ground that aluminum hydroxide was insoluble in the juices of the digestive organs. Sutton repeated Morgan's experiment, using as a dialyzer, however, a fresh sheep's bladder instead of a vegetable parchment as used by Morgan. Unlike Morgan he found no soluble aluminum compound in the dialysate. Luff cites an experiment intended to prove that dried aluminum hydroxide was insoluble in hydrochloric acid of the strength found in the gastric juice.

He took this strength of acid to be 0.02 per cent. instead of 0.2 per cent., the strength taken by the prosecution. His aluminum hydroxide also was heated to 150° instead of 100°, which is generally admitted to be the highest temperature attained by the interior of a loaf while baking, and he was not sure but the hydroxide might be changed to oxyhydroxide by heating to this temperature.

The work that has been done upon this subject seems to have been devoted to the influence of the gastric digestion alone, though J. West-Knights¹ and Dunstan,² working with diastase, reached the conclusion that the presence of alum, or of insoluble aluminum salts, interferes with the amylolytic action of ptyalin. Dunstan,² it is true, states that aluminum hydroxide interferes with pancreatic digestion, but appears to describe no experiment in proof of the statement.

J. West-Knights¹ found that gluten after treatment with alum, or its insoluble compounds, is about one-half less soluble in gastric juice than pure gluten, and pure bread is almost one-third more soluble than alumed bread in the same medium.

Pitkin³ and Mallet⁴ reached the conclusion that the aluminum compounds resulting from the use of alum baking powder were soluble to some extent in the gastric juice, while Patrick⁵ found that when the dough was well mixed and bread well baked no aluminum hydroxide, resulting from the use of alum baking powder, was dissolved in the stomach of the cat. Hehner,⁶ working

¹ *Analyst*, 1880, 5, 67.

² *Ibid.*, 1893, 18, 152.

³ *J. Am. Chem. Soc.*, 1887, 9, 27.

⁴ *Chem. News*, 1884, 58, 276.

⁵ *Analyst*, 1879, 4, 207; from *Sci. Am. Sup.*

⁶ *Analyst*, 1892, 17, 201, and 1893, 18, 213.

with an artificial pepsin solution, found the detrimental influence of alum baking powder to be equal to that of alum in the digestion of egg and bread.

The suggestion has often been made that the water-soluble salts resulting from the use of an alum baking powder, such as ammonium sulphate and potassium sulphate, would be more likely to retard digestion than the insoluble aluminum compounds. It was to study this question with reference to gastric digestion, but more especially with reference to double digestion with gastric and pancreatic ferments, that we undertook the work which forms the basis of this paper.

For the preparation of samples, flour was obtained which was known to be free from alum and seven two-pound loaves were baked under our direct supervision. The bread was raised in every case by compressed yeast.

As soon as the bread was baked it was cut in thin slices, dried at a temperature of 98°, ground, and bottled.

I. DIGESTION OF BREAD FREE FROM ALUM AND ALUMINUM COMPOUNDS.

Loaf No. 1 was found to contain 12.06 per cent. of albuminoids. Portions of two grams each were subjected to several methods of digestion. The results given are the means of closely agreeing duplicate or triplicate determinations.

1. *Digestion in Pepsin Solution.*—The pepsin solution here employed is that suggested by Wilson in his modification of Stutzer's method.¹ One gram of Merck's granulated pepsin was dissolved in one liter of 0.33 per cent. hydrochloric acid. Two grams of the dried bread, which had been previously extracted with ether, were placed in a flask with 100 cc. of the acid pepsin solution, placed in a water-bath and kept at 40°, with frequent shaking, for twelve hours. The contents of the flasks were then filtered and the residue washed, dried, and kjeldahled. It was found that 93.26 per cent. of the total albuminoids in the bread were digested,

2. *Stutzer's Method.*—Two-gram portions of the bread were then digested according to Stutzer's method, except that an

¹*J. Soc. Chem. Ind.*, 10, 118. See also Patterson in Report Maryland Experiment Station, 1891.

artificial pepsin solution, as given above, was employed instead of a solution freshly prepared from the inner membrane of a hog's stomach. The residue from the pepsin digestion, after being thoroughly washed, was digested for six hours in 100 cc. of Stutzer's¹ pancreas solution. The extracted residue was then allowed to dry and the nitrogen determined by the Kjeldahl method. By this method 93.57 per cent. of total albuminoids were digested, only a slight increase over the amount digested by the pepsin solution alone.

3. *Stutzer's Method, Modified by Wilson.*²—The pepsin solution here employed was the same as in the preceding experiments. The pancreas solution was made by dissolving one and one-half grams of Merck's "absolute pure" pancreatin, and three grams of sodium carbonate in one liter of water. The well-washed residue from the pepsin digestion was digested for twelve hours in 100 cc. of this solution, with frequent stirring, a temperature of 40° being maintained in the water-bath in which the flasks were immersed. The residue was then filtered, washed, and the nitrogen determined by the Kjeldahl method.

By this method 93.21 per cent. of the total albuminoids were digested.

4. *Niebling's Method.*³—Two grams of the sample were washed with ether and introduced into a flask with 100 cc. of two-tenths per cent. hydrochloric acid. The contents of the flask were then heated to boiling and kept at that temperature for fifteen minutes, after which they were allowed to cool and were neutralized, or rendered very slightly alkaline with a solution of sodium carbonate. One hundred cc. of Stutzer's pancreas solution were then added (without previous filtration), and the flasks immersed in the water-bath, which was kept at the temperature of 37°–40° for six hours. The residues were then washed, dried, and kjeldahled.

¹To prepare this solution take one kilogram of steer's pancreas which has been freed from fat as far as possible, pass through a sausage grinder, rub up in a mortar with sand and allow to stand exposed to the air twenty-four to thirty-six hours. Then add three liters of lime water, one liter of glycerol, sp. gr. 1.23, a little chloroform, and let stand from four to six days. Press through a bag and filter through filter paper. Before using, take 250 cc., add 750 cc. water containing five grams anhydrous sodium carbonate, heat to 37° to 40° for two hours and filter. *Landw. Versuchs-Stat.*, 1889, 36, 321–328. See also U. S. Department of Agriculture, Chem. Div., *Bull.*, 13, part 8, 1028.

²*J. Soc. Chem. Ind.*, 10, 118; through Report Maryland Experiment Station, 1891, 338.

³*Landw. Jahrb.*, 1890, 19, 149–187.

The result showed that 93.28 per cent. of the total albuminoids were digested by this method.

5. *Niebling's Method, Modified.*—This method is the same as the one preceding except that the pancreatin solution given under Wilson's modification of Stutzer's method was used instead of Stutzer's pancreas solution. The sample was digested in the pancreatin solution for twelve hours. By this method, 93.21 per cent. of the albuminoids were digested.

It will thus be seen that closely agreeing results were obtained by the different methods of digestion with bread which was as free as possible from substances which might interfere with its digestion. It was next undertaken to ascertain the effect of alum on the same methods of digestion.

II. DIGESTION OF ALUMED BREAD.

For this purpose two loaves of "alumed" bread were baked. The alum, in a fine powdered state, was thoroughly mixed with the flour before the dough was made. No. 1 contained eight-tenths gram, and No. 2, 428 grams crystallized alum in the two-pound loaf. As soon as baked the bread was dried, ground, and bottled as before. Loaf No. 1 contained 11.88 per cent., and No. 2, 12.06 per cent. albuminoids in the dried sample.

1. *Digestion in Pepsin Solution.*—

| No. | Grams alum. | Per cent. digestible albuminoids. |
|---------|-------------|-----------------------------------|
| 1 | 0.8 | 89.11 |
| 2 | 4.28 | 80.98 |

From these figures it is evident that the digestion of albuminoids in a pepsin solution is greatly lessened by the presence of alum. This it is true is universally admitted, and the results of this method are merely given as confirmatory of the work of others.

2. *Stutzer's Method.*—By Stutzer's method, using, however, an artificial pepsin solution instead of the one used by Stutzer, the following results were obtained. Since all the alum would be removed by washing after the pepsin digestion in this method and the next, the amount of alum originally present was dissolved in a little water and added to the sample previous to the pancreatic digestion.

| No. | Grams alum. | Per cent. digestible
albuminoids. |
|---------|-------------|--------------------------------------|
| 1 | 0.8 | 92.56 |
| 2 | 4.28 | 92.40 |

It will be seen that these results would lead us to a conclusion entirely different, and almost contradictory, to the one which we would obtain from the results of the pepsin solution alone. Before making further comment, however, let us examine the results obtained by the other methods of digestion.

3. *Stutzer's Method, Modified by Wilson.*—

| No. | Grams alum. | Per cent. digestible
albuminoids. |
|---------|-------------|--------------------------------------|
| 1 | 0.8 | 92.21 |
| 2 | 4.28 | 92.44 |

4. *Niebling's Method.*—

| No. | Grams alum. | Per cent. digestible
albuminoids. |
|---------|-------------|--------------------------------------|
| 1 | 0.8 | 92.54 |

5. *Niebling's Method, Modified.*—

| No. | Grams alum. | Per cent. digestible
albuminoids. |
|---------|-------------|--------------------------------------|
| 1 | 0.8 | 92.74 |
| 2 | 4.28 | 92.02 |

It is evident from these results that the custom of judging the influence of alum on the digestion by its effect on the digestion in the pepsin solution alone has led to grave errors. It is evident that the presence of alum interferes materially with the gastric digestion, but the aluminum seems to be precipitated by the alkali of the pancreatic fluid, so that a portion of the digestion which should be effected by the former ferment is effected by the latter. Of course, this paper does not take into consideration the toxic properties of alum, but we are led to believe that its influence on the digestion has been greatly overestimated.

III. DIGESTION OF BREAD CONTAINING ALUMINUM HYDROXIDE.

It was next desired to ascertain the digestibility of bread which contained aluminum hydroxide but was free from the soluble salts which result from the use of baking powders. For this purpose two two-pound loaves of bread were baked, ground, and dried as before. Loaf No. 1 contained 0.54 gram of aluminum hydroxide, corresponding to about 3.24 grams of crystallized

alum. This amount might readily be obtained by the use of an alum baking powder. Loaf No. 2 contained two and one-half grams of aluminum hydroxide, a larger amount than should ever be found in bread.

This aluminum hydroxide was prepared by precipitation from an alum solution by means of ammonium hydroxide and washing with hot water till all soluble salts were removed. It was then heated to 100° till perfectly dry, and finely powdered in a mortar. The dried and powdered aluminum hydroxide was thoroughly mixed with the flour before the dough was made.

1. *Digestion in Pepsin Solution.*—As before stated, the evidence concerning the solubility of aluminum hydroxide which has been heated to 100° in the gastric juice is of the most contradictory description. Portions of two grams each of these samples were treated with 100 cc. of the acid pepsin solution with the following results:

| No. | Grams aluminum hydroxide. | Per cent. digestible albuminoids. |
|---------|---------------------------|-----------------------------------|
| 1 | 0.54 | 87.03 |
| 2 | 2.50 | 86.78 |

According to these results the presence of aluminum hydroxide interferes materially with the digestion of albuminoids in a pepsin solution. We notice, however, that this retarding influence is not by any means proportional to the amount of hydroxide present. Indeed, although widely differing quantities of hydroxide were taken, their effect seems to be approximately the same. It seems probable, therefore, that even a much smaller amount of aluminum hydroxide might have given approximately the same results as the amounts employed. Concerning this point Hehner¹ found that when only a small amount of aluminum hydroxide was present its detrimental influence on the pepsin digestion was equal to that of an equivalent amount of alum, but when a larger amount was taken its effect was relatively less.

2. *Stutzer's Method.*—As before, a solution of Merck's granulated pepsin was used in this method in place of Stutzer's pepsin solution. The following results were obtained:

| No. | Grams aluminum hydroxide. | Per cent. digestible albuminoids. |
|---------|---------------------------|-----------------------------------|
| 1 | 0.54 | 92.18 |
| 2 | 2.50 | 90.43 |

¹ *Analyst*, 1892, 18, 213.

3. *Stutzer's Method, Modified by Wilson.*—

| No. | Grams aluminum hydroxide. | Per cent. digestible albuminoids. |
|---------|---------------------------|-----------------------------------|
| 1 | 0.54 | 92.00 |
| 2 | 2.50 | 90.21 |

4. *Niebling's Method.*—

| No. | Grams aluminum hydroxide. | Per cent. digestible albuminoids. |
|---------|---------------------------|-----------------------------------|
| 1 | 0.54 | 91.77 |
| 2 | 2.50 | 89.13 |

5. *Niebling's Method, Modified.*—

| No. | Grams aluminum hydroxide. | Per cent. digestible albuminoids. |
|---------|---------------------------|-----------------------------------|
| 1 | 0.54 | 91.90 |
| 2 | 2.50 | 88.96 |

Methods 4 and 5 give results which are noticeably lower than were obtained by the other methods. Their lack of agreement with each other also is such as to cause a serious error if these methods were adopted for this work.

These results make it evident that with aluminum hydroxide, as with alum, the results by the pepsin digestion alone cannot be taken as a guide to the influence of the aluminum hydroxide resulting from the use of an alum baking powder on the digestion. Here, as with alum, the albuminoids whose digestion is prevented in the pepsin solution by dissolved aluminum compounds, seem to be almost all digested by the alkaline pancreas solution. It is true that the digestion is not quite as complete in the presence of alum or aluminum hydroxide as in their absence. It is possible that this is due to the presence of sodium aluminate in the pancreas solution.¹ Although it appears that the influence exerted on the digestion of albuminoids by aluminum hydroxide is very slight, the possible toxic effects of even the slight amount of aluminum chloride produced in the gastric juice should not be overlooked.

IV. DIGESTION OF BREAD CONTAINING ALUMINUM PHOSPHATE.

It seems to have been quite generally assumed that aluminum phosphate was much less soluble in the gastric juice than aluminum hydroxide, and that it would exert a correspondingly less influence on digestion. Indeed, some have gone so far as to

¹ See Dunstan, *Analyst*, 1893, 18, 152.

state that the only influence which could be exerted by the compounds resulting from an aluminum phosphate baking powder must be due to the soluble salts. In order to determine the effect of aluminum phosphate in the absence of the soluble salts, the preceding set of digestions was repeated with bread containing aluminum phosphate. Two two-pound loaves of bread were baked with the addition of aluminum phosphate and prepared for analysis as before. Loaf No. 1 contained 0.64 gram of aluminum phosphate, which is equivalent to 2.56 grams of crystallized alum. This amount has frequently been found in bread prepared by alum baking powder. Loaf No. 2 contained 3.20 grams of aluminum phosphate, an amount largely in excess of that usually found in bread.

For the preparation of this compound, alum was dissolved in water, an excess of hydrogen disodium phosphate added, and the resulting precipitate washed with water until the filtrate ceased to be acid. It was then dried at 100° and reduced to a fine powder in a mortar. The dried and powdered aluminum phosphate was thoroughly mixed with the flour before the dough was made.

1. *Digestion of Pepsin Solution.*—Portions of the samples were digested in the acid pepsin solution, as before, after washing with ether to remove the fat. The following results were obtained:

| No. | Grams aluminum phosphate. | Per cent. digestible albuminoids. |
|---------|---------------------------|-----------------------------------|
| 1 | 0.64 | 80.87 |
| 2 | 3.20 | 71.21 |

Comparing the result obtained in sample 1 with that obtained by the peptic digestion of alumed bread, we find that even when a relatively large amount of aluminum phosphate is present, its effect on the pepsin digestion is equal to that of an equivalent amount of alum. It is also apparent that its effect is much greater than that of an equivalent amount of hydroxide.

2. *Stutzer's Method.*—As in the previous digestions, this method was modified by substituting a solution of Merck's granulated pepsin for Stutzer's pepsin solution. The following results were obtained:

| No. | Grams aluminum phosphate. | Per cent. digestible albuminoids. |
|---------|---------------------------|-----------------------------------|
| 1 | 0.64 | 83.11 |
| 2 | 3.20 | 78.26 |

3. *Stutzer's Method, Modified by Wilson.*—

| No. | Grams aluminum
phosphate. | Per cent. digestible
albuminoids. |
|---------|------------------------------|--------------------------------------|
| 1 | 0.64 | 82.56 |
| 2 | 3.20 | 81.32 |

4. *Niebling's Method.*—

| No. | Grams aluminum
phosphate. | Per cent. digestible
albuminoids. |
|---------|------------------------------|--------------------------------------|
| 1 | 0.64 | 86.35 |
| 2 | 3.20 | 82.18 |

These results differ materially from those obtained by the other methods of digestion.

5. *Niebling's Method, Modified.*—

| No. | Grams aluminum
phosphate. | Per cent. digestible
albuminoids. |
|---------|------------------------------|--------------------------------------|
| 1 | 0.64 | 86.46 |
| 2 | 3.20 | 81.74 |

These results agree fairly closely with those obtained by method 4, but are materially lower than those obtained by methods 2 and 3.

From these results it appears that the influence of aluminum hydroxide on the digestibility of bread is about the same as that of an equivalent amount of alum, when present in about the quantity which is usually found as a result of the use of alum baking powder which contains no phosphate.

The action of aluminum phosphate is quite different, however, for notwithstanding the supposed insolubility of this compound, ten to twelve per cent. of the albuminoids which are digestible in the presence of alum or aluminum hydroxide appear to be insoluble in the presence of an equivalent amount of the phosphate.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY.—No. 9.]

SOME CHARACTERISTICS OF CALIFORNIA WINES.

By W. H. KRUG.

AMONG the exhibits of American products at the World's Columbian Exposition, at Chicago, in the year 1893, one of the most interesting and varied was that of the California wine producers at the California State Building. The wines shown there, represented all the important districts in the state and the various types grown. At the suggestion of Dr. H. W. Wiley, Chief Chemist of the U. S. Department of Agriculture, the Cali-

for California viticultural commission sent a set of these wines to the laboratory of the department, where they were analyzed under my supervision. All important varieties were represented and the analyses were made as complete as possible. The wines were classified as follows:

DRY WHITE WINES—36 of the Rhenish type.
38 of the Sauterne type.
6 of the white Burgundy type.
7 miscellaneous.

DRY RED WINES—37 of the Claret type.
22 of the Medoc type.
20 of the Burgundy type.

SWEET OR FORTIFIED WINES—6 of the Sherry type.
13 of the Port type.
9 miscellaneous.

—In toto, 194.

GENERAL REMARKS.

California wine producers grow European types almost exclusively, and it will be seen from the table of analyses that they aim to follow these types in their description as closely as possible. This is carried even to the extent of adopting the various styles of bottles used in the European trade.

A few of the white wines were considerably deeper in color than the European wines of the same type. By far the greater number, however, were perfectly clear and brilliant, showing that great care had been exercised in maturing and preparing for bottling. This was especially true of the red wines. The following determinations were made:

Specific gravity, alcohol by weight, alcohol by volume, extract, total acidity as tartaric acid, polarization of 26.048 grams in a 200 mm. tube, polarization of the wine in a 220 mm. tube, Wild polariscope, reducing sugar as dextrose, glycerol, tannin and coloring matter, albuminoids, ash, sulphuric acid in ash, potassium sulphate in 100 cc. of wine stated in grams, chlorine in ash, sodium chloride in 100 cc. of wine stated in grams, insoluble residue in ash, sulphurous acid and salicylic acid.

In the sweet wines, the polarization was determined after inversion and after fermentation, the result being stated both in terms of 26.048 grams and of the original sample. The work on the

color intensity, and the presence of foreign coloring matters, has been delayed unavoidably and will not be ready in time for incorporation in this paper. It is intended to make this branch of the investigation especially complete.

METHODS OF ANALYSIS.

Specific Gravity.—The specific gravity was taken on an analytical balance by means of a Westphal bob whose displacement had been previously determined.

Alcohol.—One hundred cc. of the wine were placed in a flask with fifty cc. of water and a little precipitated calcium carbonate, the flask attached to an upright condenser and the contents of the flask subjected to distillation. To prevent the volatilization of the alcohol, the condenser tube should be made to extend almost to the bottom of the receiver. A 100 cc. flask was used for a receiver, and when 100 cc. of the distillate had passed over, the operation was interrupted and the flask removed, shaken, and the specific gravity of the distillate determined in the same manner as given under specific gravity. The percentage of alcohol by volume was determined from the specific gravity by table II, on page 213, in Bulletin 38, Division of Chemistry, U. S. Department of Agriculture, and the percentage of alcohol by weight was determined by multiplying the percentage of alcohol by volume, by the specific gravity of absolute alcohol and dividing that product by the specific gravity of the wine.

Extract.—The direct method was used. In the case of dry wines, fifty cc. were weighed and evaporated on the water-bath to a sirupy consistence in a platinum dish about eighty-five mm. in diameter. The residue was dried two and one-half hours in a drying oven at 100°. Of the sweet wines only ten cc. were weighed and diluted with distilled water before being evaporated.

Total Acidity (expressed as tartaric acid).—Ten cc. of the wine were carefully measured into a beaker, diluted with distilled water, and a few drops of neutral litmus solution added. Decinormal sodium hydroxide solution was used in the titration, and the neutral point was determined by placing a drop of the liquid on delicate litmus paper. This was found to work equally well on white and red wines. A standard solution of calcium hydrox-

ide has been recommended for red wines, the end reaction being the appearance of a flocculent precipitate. I found it much more difficult, however, to observe this than to note the neutral point with sensitive litmus paper. Before this point is reached the natural coloring matter of the wine will change, indicating the approach of neutrality so that the operator can work without difficulty to within a tenth of a cubic centimeter.

Glycerol.—A. In dry wines. One hundred cc. of wine were evaporated down to about ten cc. on the water-bath with about five grams of fine sand. Milk of lime was then added until the reaction was strongly alkaline, and the evaporation carried almost to dryness. The residue was gently heated on the water-bath with about fifty cc. of ninety-six per cent. alcohol, and mixed with a glass pestle until a homogeneous paste was obtained. It was allowed to settle and the supernatant liquid filtered through a folded filter. The residue was repeatedly extracted in this manner until about 150 cc. of filtrate were obtained. To this a few pieces of glass or sand were added to prevent bumping, and the alcohol carefully distilled off over a small flame until about fifteen cc. remained. The evaporation was then continued on the steam-bath until the residue became sirupy. After cooling, it was dissolved in ten cc. of absolute alcohol and fifteen cc. anhydrous ether added, the flask well-stoppered and shaken. When the precipitate had collected on the sides of the flask, the clear liquid was decanted into a tared glass-stoppered weighing bottle capable of holding about fifty cc., the precipitate washed once or twice with a few cc. of a mixture of two parts of alcohol and three of ether, the washing being transferred to the weighing bottle. The ether-alcohol removed on the water-bath, the residue dried one hour in a water-oven and weighed. When the precipitate, caused by the addition of the ether, remains flocculent, it is separated by filtering through a small filter, which is then washed repeatedly with a few cc. of the ether-alcohol mixture.

B. In sweet wines. One hundred cc. of the wine are evaporated to a thick sirup on the water-bath with about ten grams of sand. The residue is repeatedly extracted with absolute alcohol until from 100 to 150 cc. have been used (the amount being

varied with the amount of sugar present). The extracts are united in a large flask and one and one-half parts ether added for every part of alcohol used. The flask is stoppered and allowed to stand until the liquid is clear. Almost all the sugar is present in the sirupy precipitate while the glycerol remains in solution. The clear liquid is decanted into a flask, the residue washed repeatedly with small quantities of the ether-alcohol mixture and the united liquids distilled. The evaporation is completed on the water-bath, the residue washed into a porcelain dish by means of a little water, and treated as in A.

Polarization.—The wines were all polarized in a Schmidt and Haensch instrument with a 200 mm. tube. In the case of the dry wines, fifty cc. were evaporated sufficiently to permit the addition of three cc. of lead subacetate solution and three cc. of a saturated sodium carbonate solution to the white, and respectively six cc. of each solution to the red wines. The precipitate was filtered off and the filtrate polarized. In the case of the sweet wines twenty-five cc. were taken and made up to fifty cc.

The sweet wines were both inverted and fermented. For inversion twenty-five cc. were placed in a fifty to fifty-five cc. flask, two and one-half cc. strong hydrochloric acid added. The flask was heated in a water-bath to 68° C., consuming about ten minutes in heating. It was removed, cooled quickly to room temperature, filtered, and polarized. For fermentation, fifty cc. were placed in a wide-mouthed flask, a quarter of a cake of Fleischmann's compressed yeast and a sufficient amount of a potassium fluorid solution added, so that ten mgms. of this salt were present. The flask was allowed to stand four days at room temperature when it was found that fermentation was complete. The liquid was then washed into a 100 cc. flask, four cc. of lead subacetate solution, two cc. of mercuric nitrate solution (U. S. Department of Agriculture, Division of Chemistry, Bulletin 38, p. 198), and a varying amount of thick alumina cream added. It was then made up to 100 cc. with water, filtered, and polarized. The mercuric nitrate solution was added to destroy any bacteria which might impair the transparency of the filtrate when the latter, by any chance, stood for a length of time before being polarized.

If, after inversion, the wine polarizes more strongly to the left, unfermented cane sugar is present.

If, after fermentation, it polarizes to the right, the unfermentable constituents of commercial glucose are probably present.

Reducing Sugar.—This was determined by Allihn's gravimetric method and was calculated as dextrose.

Reagents.—1. 34.639 grams of crystalline copper sulphate dissolved in water and diluted to 500 cc.

2. One hundred and seventy-five grams of Rochelle salt.

One hundred and twenty-five grams of potassium hydroxide.

Dissolved in water and diluted to 500 cc.

In white wines. Fifty cc. were neutralized with sodium carbonate, the alcohol removed by heating on the steam-bath, made up to the original volume with water and filtered through a dry filter. When necessary, this solution was diluted with water to bring the reducing sugar down to one per cent. or less.

Thirty cc. of the copper solution, thirty cc. of the seignette solution, and sixty cc. of water, were placed in a beaker and heated to boiling. Twenty-five cc. of the sugar solution were then added and the whole boiled two minutes. The cuprous oxide was immediately filtered off and washed with hot water. It was then dissolved in dilute nitric acid, reduced to copper by the usual electrolytic method and weighed in that form.

The red wines were decolorized by filtering through bone-black, the first portion being rejected and the second portion treated precisely as the white wines.

Tannin and Coloring Matter.—The Löwenthal method was used.

Reagents.—Permanganate of potash solution: 1.333 grams of crystallized potassium permanganate in a liter of water.

Indigo solution: Six grams of sodium indigo sulphate and fifty cc. concentrated sulphuric acid per liter of water.

Decinormal oxalic acid solution.

Washed bone-black suspended in water so as to make a thin paste.

A. One hundred cc. of wine were dealcoholized by boiling and the lost weight restored with water. Ten cc. of the dealcoholized wine are transferred to a large porcelain casserole, twenty

cc. of the indigo solution and about 750 cc. of distilled water added, and the titration carried out with the permanganate solution, adding a cubic centimeter at a time until the liquid becomes green, when it is added drop by drop until the color turns to golden-yellow. Result A.

B. Ten cc. of the dealcoholized wine are diluted with water, a few cc. of the bone-black added, the liquid well stirred with a glass rod and allowed to stand some time. The bone-black is then filtered off and washed repeatedly with water. The filtrate is diluted to about 750 cc. and titrated as in A after adding the indigo solution. Result B.

Result A—Result B=cubic centimeters required by the tannin and coloring matter. This is stated in terms of oxalic acid.

Ash.—The residue from the extract determinations was carefully incinerated and weighed. In the sweet wines, the ash was determined by charring the extract and exhausting with hot water. The insoluble residue, consisting mostly of carbon, was collected on a filter, washed, dried, and burnt separately, the residue from the water extract was added to this and the whole heated to low redness until white.

Albuminoids.—The Kjeldahl method was used, the wine being previously evaporated to dryness in the digestion flasks. The amount used varied with the wines, it being necessary to use as little as ten cc. of some of the sweet wines on account of the tendency to foam when digested with sulphuric acid.

Sulphuric Acid and Chlorine in the Ash.—The ash was digested with hot water and a few drops of nitric acid and filtered into a fifty cc. flask. The residue was washed with hot water until the flask was full to the mark. It was cooled, made up and the sulphuric acid estimated in an aliquot portion in the usual manner. In another portion the chlorine was determined volumetrically with $\frac{N}{200}$ silver nitrate solution. They were respectively converted to grams potassium sulphate and sodium chloride in 100 cc. of wine.

Insoluble residue in Ash.—The filter and residue were ignited in a weighed platinum crucible and weighed.

Sulphurous Acid.—In the determination of sulphurous acid 100 cc. of the wine were diluted in a distilling flask with fifty

cc. of water, acidulated with five cc. of dilute sulphuric acid (H_2SO_4 one part, H_2O three parts). The distillation was carried on in an atmosphere of carbon dioxide and the distillate received in a flask containing a measured quantity of decinormal iodine solution. The condenser tube should extend well below the surface of the iodine solution and in case a current of carbon dioxide be passed through the apparatus, the receiving flask should be closed with a mercury valve or attached to a U tube containing a portion of the iodine solution. In the progress of the work it was found more convenient to expel the atmosphere by the addition of a small quantity of sodium carbonate and in this case the guard-tube was found to be unnecessary. After about 100 cc. have distilled over, the excess of iodine is determined with decinormal sodium thiosulphate solution.

Salicylic Acid.—The following method was worked out by Mr. W. D. Bigelow who had charge of this branch of the investigation.

Seventy-five cc. of the wine are placed in a separatory funnel, acidified with five cc. of dilute sulphuric acid (H_2SO_4 one part, H_2O three parts) and extracted with a mixture of eight parts of sulphuric ether and one part of petroleum ether. The ether is washed once with water and then thoroughly shaken with about twenty-five cc. of water and six to eight drops of a five-tenths per cent. solution of ferric chloride. The aqueous layer contains most of the coloring matter in combination with the iron and is discarded. The ether is then washed with water, transferred to a porcelain dish, evaporated to dryness and the residue heated to the full temperature of the steam-bath for a few minutes. When the dish has become cool from four to five cc. of water are added, the insoluble matter filtered off after a few minutes and the filtrates tested for salicylic acid by the addition of three to four drops of a five-tenths per cent. solution of ferric chloride. By this method an excellent clarification may be obtained with white wines and with most red wines. Sometimes, however, with the latter, a second extraction is necessary.

GENERAL REMARKS CONCERNING THE METHODS OF JUDGMENT.

There being no law in this country which governs and regu-

lates the chemical composition of wines it was deemed advisable to apply some foreign standard. It is true that our wines grown under different climatic and soil conditions cannot be judged with absolute fairness by a standard based on the composition of European natural wines. Such application can only be of value as a means of comparison and was applied only in such sense.

The standards used were those adopted in the German Empire. On account of the lengthiness of the report made by the Royal Commission empowered to frame the regulations, I will only mention the more salient points relating to the constituents of wine. They are as follows:

Wines which have been prepared solely from pure grape juice contain only rarely less than one and one-half grams extract per 100 cc. If, therefore, a wine is found to contain less it must be rejected unless it can be proved that other wines of the same type and year exhibit the same peculiarity.

After deduction of the "fixed acid" the extract-rest in natural wines equals at least one and one-tenth grams per 100 cc., after deduction of the total acid at least one gram.

A wine in which the ash equals more than ten per cent. of the extract, should contain a correspondingly larger amount of extract than is usually assumed to be a minimum. In natural wines the ash and extract are very often found to be in the proportion of one to ten. A considerable variation from this ratio, however, does not justify the assumption that the wine is adulterated.

In accordance with experience the free tartaric acid does not amount to more than one-sixth of the "fixed acids."

The ratio between glycerol and alcohol can vary in natural wines from 7:100 to 14:100. Wines having a different ratio have had either alcohol or glycerol added to them.

As during the various manipulations which the wine undergoes, small amounts of alcohol (not more than one per cent. volume) may get into the wine, this must be considered in judging wines. The above limits and ratios are not always applicable to sweet wines.

For the individual inorganic constituents no reliable limits

can be given. The supposition that better wines always contain more phosphoric acid is without foundation.

Wines containing less than 0.14 gram ash per 100 cc. must be rejected unless it is shown that other natural wines of the same type and year show the same peculiarity.

Wines containing more than 0.05 gram NaCl in 100 cc. must be rejected.

Wines containing more than 0.092 gram of SO_2 per 100 cc. (corresponding to two grams of K_2SO_4 per liter) must be designated as having been treated with gypsum, *i. e.*, plastered.

Various circumstances or influences can make a wine ropy, dark, brown, turbid, or bitter, or can change its color, taste, and odor. The coloring matter of red wines may thus be precipitated. None of the above phenomena justify the assumption that the wine is not genuine.

A second fermentation in a wine does not absolutely indicate the addition of sugar or sweet substances. Very often the original fermentation is hindered, or a sweet wine may have been added to the original completely fermented wine.

In only a few samples were deposits noticeable, most of the wines, both white and red, presenting a fine appearance and showing that they were well-matured before being bottled. Deposits were much more prevalent among the white than among the red wines. In the analytical tables, the wines are classified by types, and this classification is followed in the discussion as far as practicable.

To facilitate discussion of the results the most important points were arranged as follows:

1. Are substances present which are not characteristic of pure natural wines and deleterious to health?
2. Is the quantitative composition of the wines such as is shown by European natural wines?
3. In what manner have the manipulations varied from those used in the preparation of pure natural wines?

First.—Are substances present which are not characteristic of pure natural wines and deleterious to health?

Such substances may be unfermented cane sugar, the unfermentable constituents of glucose, potassium sulphate, sodium

chloride, sulphurous acid, and other preservatives. Some interesting data were obtained in this connection.

Among the twenty-eight sweet wines there was only one, Port, No. 12,814, that gave a zero polarization after fermentation. In every other instance, as will be seen from the tables, there was a dextro rotation showing possibly that commercial glucose had been used for purposes of fortification. It is well-known, however, that this substance is not used in California, and, therefore, this dextro rotation is not positive proof of the use of glucose. All but five gave an increased left-handed reading after inversion, indicating the presence of non-inverted sucrose. Although there can be no objection to the presence of sucrose or invert sugar, it has not been determined as yet whether the unfermentable constituents of glucose, the most important of which is amylin, exert any specific physiological action on the human body, and as long as this is the case any decision on their injuriousness must be withheld.

To produce sweet wines it is absolutely necessary to add some saccharine substance to obtain the desired strength in alcohol and requisite sweetness. It would be much more rational, however, for the producer to use cane sugar, which can be procured pure so easily, especially as it has hitherto been impossible to obtain pure dextrose at a price which would render its use profitable.

There were found only three wines which exceeded the German limit for potassium sulphate; namely, Gutedel, No. 12,678, with 2.321 grams per liter, Zinfandel, No. 12,713, with 2.392 grams per liter, and Burgundy, No. 12,714, with 2.315 grams per liter, the latter two being from the same winery. Plastering is therefore not used very much to excess by California wine producers. Plastering is the commercial term applied to the treatment of the grapes with burnt gypsum. All Spanish, Italian, and Greek wines are extensively plastered. In Greece, a layer of grapes is placed in a low cistern and well-covered with gypsum, which is followed with another layer of grapes in turn covered as before, this being continued until the cistern is full. After from twelve to twenty-four hours the grapes are mashed by treading and the must filled in casks. The use of gypsum

secures a quicker ripening and better color. The chemical changes taking place are, in brief, as follows:

The potassium bitartrate and calcium sulphate react forming calcium tartrate and potassium acid sulphate, of which the former, on account of its insolubility, separates almost entirely during fermentation. This insolubility is also the cause of the rapid clearing of the wine after fermentation. The improved color of a wine thus treated is stated by Kayser to be due to the presence of free phosphoric acid. Plastering has become very popular in France, as it enables the producers to supply a cheap red wine by avoiding the expense attached to a long period of ripening. Plastered wine contains the same amount of potash as the must, while in a natural wine the precipitation of potassium bitartrate decreases the potash more or less. Pure must contains rarely as much as two-tenths gram of SO_2 per liter, while in plastered wines this is greatly exceeded, often amounting to eight-tenths to two grams per liter. Plastered wines always show a higher ash than natural wines. Thus a wine of from eight to ten volume per cent. alcohol and 2.2–2.3 grams extract per 100 cc., which normally contains 0.2–0.25 gram of ash per 100 cc. will, after plastering, contain 0.28–0.35 gram. A plastered wine made from pure must will always contain at least one-tenth gram of potash per 100 cc., and usually considerably more.

From a physiological standpoint the only objection to plastered wines is the presence of potassium sulphate. Although it is evident that the consumption of a large quantity of such wines would be necessary to produce a physiological action on a normal individual, it must likewise be considered that much smaller quantities may be harmful to invalids and children. When we keep the fact in mind that the southern sweet wines are the ones preferred for medicinal use, and at the same time the ones most extensively plastered, we can appreciate the force of these remarks. None of the California sweet wines analyzed exceeded the limit, two grams per liter, although one, Port, No. 12,710, approached it with 1.861 grams per liter.

All the dry white and the sweet wines, with the exception of the Ports and Sherries, were examined quantitatively for sul-

phurous acid and only twelve were found that contained none. In every other case the amount present exceeded the limit placed by the German law. Even when we adopt the limit suggested by the Association of Bavarian Representatives of Applied Chemistry; namely, 0.01 gram per liter, we find that all the wines analyzed that were found to contain sulphurous acid exceed this by far. They are sulphured excessively. Sulphuring is, without doubt, one of the most important adjuncts to the manufacture of wine.

The use of sulphurous acid is very old. Arnolf de Villanova mentions it in his work on wine manufacture printed in 1830 and von Holburg in 1587 recommended the use of sulphur to fumigate the casks and directed to burn three sticks and then close the cask so as to retain the fumes. He found that this insured good and perfect wines that did not deteriorate on standing. In a book published in Nuremberg in 1708 entitled "Der Kuriose Kellermeister," the amount of sulphur required for a 600 liter cask is given as seventeen grams. In a book published in 1775 under the title "Treatise on the Improvement of Wine and the Prevention of Injurious Practices in Wine Making." This statement is made on page 75: "Fumigation is necessary and important, first to preserve the wines and cask and second to improve the wine."

Only twice have attempts been made to replace sulphur. Once when the use of alcohol was suggested and again when it was believed that an ideal preservative had been found in synthetic salicylic acid. Neither realized the expectations of its promoters and sulphuring to-day still holds the same position that it has for centuries. Sulphuring is used to fumigate the casks, to prevent oxidation in the wines, and to prevent diseases peculiar to the wines.

Technically the use of sulphur is, without doubt, wrong. Wine ages by a slow process of oxidation which is absolutely interrupted as long as any sulphurous acid is present. As a preservative, sulphurous acid in the amount used is not an unqualified success as is shown by the necessity of repeating sulphuring when a wine stands for some time before being consumed. Nessler found that from thirteen to eighty-one mgms.

per liter were required to prevent the browning and turbidity of red wines. Moritz found that the growth of *mycoderma vini* was not indefinitely hindered until 0.05 per cent. sulphurous acid was present. All these figures far exceed the limits of the European laws.

From a physiological standpoint the presence of sulphurous acid is objectionable not so much on account of any possible immediate action but more through the cumulative effect on the digestive tract. Such effects will rapidly become general throughout the whole nervous system. In connection with this the experiments of Braun and Bematzik are of interest. They are the only ones made on man and showed that doses of eighty mgms. upwards caused serious irritation of the alimentary canal. Husemann and Bischoff recorded several cases where the consumption of freshly sulphured wine caused physiological disturbances and severe headache in persons otherwise accustomed to wine.

A further objection is the formation of bisulphates and even of free sulphuric acid in frequently sulphured wine. These also have a physiological action which cannot well be overlooked.

Eighty-seven wines were examined for sulphurous acid. Thirty-three of those contained more than eighty mgms. sulphurous acid per liter. Of these twenty-nine contained over 100 mgms., nine of 200 mgms., and two over 300 mgms.

All wines were examined for salicylic acid and only four were found to contain this preservative; namely, Sauterne No. 12,631, heavy reaction; Claret No. 12,633, very heavy; Port No. 12,627, distinct; and Port No. 12,710, heavy. It is hardly necessary to explain the objections against this preservative and it is a pleasure to find it so little used by wine producers in California. Nos. 12,627, 12,631, and 12,633 are wines from the same firm.

Second.—Is the quantitative composition of the wines such as is shown by natural wines?

All the wines analyzed show when compared with European wines one striking difference, their much lower glycerol-alcohol ratio. According to the German law this should not be lower than seven nor higher than fourteen, sweet wines to be excepted. A glance at the analyses will show that in California wines it

rarely rises to eight or above and that the average is from five to six. Baumert in his work on seven California wines also found this to be the case and makes the assertion that it is due to a slight alcoholizing of the wines. In our work we have, however, found it to be a general characteristic and it hardly seems possible that wine producers should practice this mode of fortification so universally. I am rather inclined to believe that the proper solution of the problem will be found in a careful study of the processes of fermentation as they take place in the California wines. It is probable that the fermentation takes place too rapidly to permit of the formation of a proper quantity of glycerol.

A comparison between the composition of California wines and European wines of the same type is difficult as the propriety of applying the same form of judgment to two kinds of wine grown under different conditions of soil and climate is doubtful. Still it may be of interest to call attention to the points wherein they differ.

For purposes of comparison the analyses given in König, *Chemie der menschlichen Nahrungs-und Genussmittel* were used.

Wines of the Rhenish Type.—The California Riesling is distinguished according to these analyses by a higher alcohol and lower extract content, and a somewhat lower acidity. The percentage of glycerol present is in most cases much lower. The California Riesling varies from 8.45–11.67 per cent. alcohol by weight, 1.66–2.61 per cent. extract, 0.478–0.658 per cent. total acid as tartaric acid, and 0.501–0.932 per cent. glycerol, while German Riesling varies from 5.90–10.15 per cent. alcohol by weight, 1.7–3.21 per cent. extract, 0.395–1.250 per cent. total acid as tartaric acid, and 0.49–1.34 per cent. glycerol.

California Gutedel, on the other hand, is higher both in alcohol and extract, while the acidity is somewhat lower. It varies from 9.67–11.16 per cent. alcohol by weight, 1.67–2.34 per cent. extract, and 0.467–0.662 per cent. total acidity. German Gutedel shows from 7.12–8.23 per cent. alcohol by weight, 1.67–2.01 per cent. extract and 0.241–0.830 total acidity. The California wine shows in accordance with its higher percentage of extract a higher ash than the German wine.

No analyses of German Hock could be found, so it is impossible to draw comparisons on this wine, though its close agreement with the two wines just discussed makes it highly probable that it will exhibit the same characteristics. In general, these wines are all somewhat stronger in alcohol and higher in extract than the German wines of the same type.

Wines of the Sauterne Type.—A comparison of the minima and maxima and means of American Sauterne with those of French Sauterne show that although the average California Sauterne shows a higher alcohol content, wines are found on the French market that exceed the highest found in our work. California Sauterne shows a lower extract and acidity, while the percentage of glycerol is far below that found in French wines. The following figures will exhibit this. California Sauterne: Alcohol by weight, 8.43–12.18 per cent., extract, 1.7–4.03 per cent., acidity, 0.422–0.641 per cent., and glycerol, 0.178–0.850 per cent. French Sauterne: Alcohol by weight, 9.05–12.49 per cent., extract, 2.47–3.54 per cent., acidity, 0.54–0.75 per cent., and glycerol, 0.866–1.03 per cent.

The same general characteristics are true of the other miscellaneous California white wines analyzed. On the whole, all these wines exhibit a higher alcohol, somewhat lower extract and acidity, and a much lower percentage of glycerol.

Wines of the Claret Type.—The various California representatives of the Claret type, the most important of which is the Zinfandel, all show a higher percentage of alcohol, extract and total acid, and a lower glycerol content than the French Clarets. California Zinfandel shows the following minima and maxima: Alcohol by weight, 9.15–10.5 per cent., extract, 2.28–3.37 per cent., total acidity, 0.635–0.871 per cent., glycerol, 0.446–0.634 per cent. California Claret gives the following figures: Alcohol by weight, 9.16–11.23 per cent., extract, 2.36–3.34 per cent., total acidity, 0.601–0.783 per cent., and glycerol, 0.484–0.620 per cent. French Clarets vary within the following limits: Alcohol by weight, 7.45–9.32 per cent., extract, 2.0–3.0 per cent., total acidity, 0.47–0.78 per cent., and glycerol, 0.55–0.99 per cent. In accordance with the higher extract a higher ash was found in California Clarets; *viz.*, 0.235–0.342 per cent., French Clarets giving 0.19–0.31 per cent.

Wines of the Medoc Type.—These wines are represented in California by the Cabernet, Malbec and Medoc. Only the last could be compared with French wines, no analyses of wines of the first two subtypes being found. Here it was again found that the California wines were characterized by a higher percentage in alcohol, extract and acidity, while the glycerol was much lower than in the French Medocs.

The following minima and maxima were obtained. California Medocs: Alcohol by weight, 11.75–12.4 per cent., extract, 2.33–2.92 per cent., acidity, 0.614–0.824 per cent., and glycerol, 0.371–0.556 per cent. French Medocs: Alcohol by weight, 9.50–10.70 per cent., extract, 1.96–2.60 per cent., total acidity, 0.380–0.680 per cent., and glycerol, 0.640–1.04 per cent. Corresponding to the higher extract a higher ash was found in the domestic wines; *viz.*, 0.304–0.386 per cent. French Medocs showing from 0.21–0.297 per cent.

Wines of the Burgundy Type.—Only one analysis of a Burgundy wine was in König. A comparison with this showed the California Burgundies to contain a higher percentage of alcohol, extract, acidity, and ash than French Burgundy, while the glycerol is lower. The following minima, maxima, and means were obtained:

CALIFORNIA BURGUNDY.

| | Minimum.
Per cent. | Maximum.
Per cent. | Mean.
Per cent. |
|------------------------|-----------------------|-----------------------|--------------------|
| Alcohol by volume..... | 10.97 | 15.48 | 12.57 |
| Extract..... | 2.20 | 3.48 | 2.79 |
| Acidity | 0.594 | 0.783 | 0.674 |
| Ash..... | 0.190 | 0.362 | 0.283 |
| Glycerol | 0.464 | 0.640 | 0.551 |

CALIFORNIA MATARO.

| | Minimum.
Per cent. | Maximum.
Per cent. | Mean.
Per cent. |
|------------------------|-----------------------|-----------------------|--------------------|
| Alcohol by volume..... | 9.58 | 13.40 | 12.38 |
| Extract..... | 2.24 | 3.39 | 2.79 |
| Acidity | 0.601 | 0.837 | 0.673 |
| Ash..... | 0.203 | 0.322 | 0.278 |
| Glycerol | 0.544 | 0.583 | 0.553 |

French Burgundy: Alcohol by volume, 11.23 per cent., extract, 2.63 per cent., acidity, 0.390 per cent., ash, 0.210 per cent., and glycerol, 0.680 per cent.

A general comparison of all California dry wines shows, therefore, that they are characterized by a high percentage of alcohol and low percentage of glycerol. In the white wines, the extract, acidity and ash are generally lower than in foreign wines while in the red wines these constituents are higher.

SWEET WINES.

Wines of the Sherry Type.—California Sherries on the whole are lower in alcohol than Spanish Sherries. They are higher in extract, which is due to the presence of unfermented grape sugar. The total acidity is higher while the ash and glycerol are lower. Following are the minima and maxima: California Sherry: Alcohol by weight, 14.38-17.57 per cent., extract, 3.33-9.38 per cent., acidity, 0.378-0.797 per cent., reducing sugar, 1.20-6.17 per cent., ash, 0.211-0.420 per cent., and glycerol, 0.325-0.722 per cent. Spanish Sherries: Alcohol by weight, 16.01-19.88 per cent., extract, 2.69-5.40 per cent., acidity, 0.250-0.640 per cent., reducing sugar, 0.52-3.77 per cent., ash, 0.200-0.660 per cent., glycerol, 0.220-0.910 per cent.

Wines of the Port Type.—These wines exhibit in general the same characteristics in comparison with Portuguese Ports as the Sherries; namely, a slightly lower percentage of alcohol, and a higher extract and acidity. The glycerol is in these wines slightly higher. The high extract is due to the presence of unfermented grape sugar. The following data were obtained: California Ports: Alcohol by weight, 11.97-17.40 per cent., extract, 8.52-16.51 per cent., acidity, 0.412-0.674 per cent., reducing sugar, 5.16-13.00 per cent., and glycerol, 0.161-0.688 per cent. Portuguese Ports: Alcohol by weight, 15.71-17.87 per cent., extract, 6.69-9.90 per cent., acidity, 0.290-0.470 per cent., reducing sugar, 4.42-8.12 per cent., and glycerol, 0.230-0.710 per cent.

COMPARISON OF CALIFORNIA MUSCATEL WITH OTHER WINES OF THAT NAME.

California Muscatel approaches the Syrian Muscatels in its alcohol content. No strict comparisons can be drawn between it and Sicilian Muscatels as the latter vary within too wide limits. It is stronger in alcohol and has in general a lower extract than the Greek Muscatels, due no doubt to the fact that

a large quantity of concentrated must is added to the finished wine in Greece so as to obtain a very sweet product. The glycerol content is higher and the ash and total acidity lower than in foreign Muscatels.

The following minima and maxima will show the differences existing :

CALIFORNIA MUSCATEL.

| | Minimum.
Per cent. | Maximum.
Per cent. | Mean.
Per cent. |
|-------------------------|-----------------------|-----------------------|--------------------|
| Alcohol by weight | 10.45 | 15.50 | 13.63 |
| Extract | 17.01 | 18.62 | 17.55 |
| Acidity | 0.317 | 0.405 | 0.369 |
| Reducing sugar | 43.18 | 16.30 | 14.66 |
| Glycerol | 0.866 | 1.014 | 0.941 |
| Ash | 0.148 | 0.192 | 0.113 |

SYRIAN MUSCATELS.

| | Minimum.
Per cent. | Maximum.
Per cent. | Mean.
Per cent. |
|-------------------------|-----------------------|-----------------------|--------------------|
| Alcohol by weight | 10.67 | 15.26 | 13.63 |
| Extract | 4.22 | 18.86 | 9.76 |
| Acidity | 0.430 | 0.830 | 0.646 |
| Reducing sugar | 0.25 | 4.50 | 3.13 |
| Glycerol | 0.320 | 2.00 | 0.857 |
| Ash | 0.210 | 0.960 | 0.495 |

GREEK MUSCATELS.

| | Minimum.
Per cent. | Maximum.
Per cent. | Mean.
Per cent. |
|-------------------------|-----------------------|-----------------------|--------------------|
| Alcohol by weight | 9.44 | 11.62 | 10.57 |
| Extract | 13.32 | 24.13 | 15.27 |
| Acidity | 0.410 | 0.751 | 0.566 |
| Reducing sugar | 13.50 | 18.86 | 15.01 |
| Glycerol | 0.564 | 0.950 | 0.718 |
| Ash | 0.290 | 0.388 | 0.321 |

SICILIAN MUSCATELS.

| | Minimum.
Per cent. | Maximum.
Per cent. | Mean.
Per cent. |
|-------------------------|-----------------------|-----------------------|--------------------|
| Alcohol by volume | 6.00 | 24.66 | 15.34 |
| Extract | 3.56 | 38.18 | 20.08 |
| Acidity | 0.270 | 1.140 | 0.630 |
| Reducing sugar | 12.50 | 29.01 | 17.16 |
| Glycerol | | | |
| Ash | 0.170 | 0.860 | 0.410 |

Five other samples of sweet wines were analyzed; namely, three Angelicas, one Tokay, and one Catawba. Of these, the Tokay is the most interesting as it differs in every respect from

the Hungarian Tokays. The percentages of alcohol and glycerol present are much higher; the extract, reducing sugar, acidity, and ash, lower. It is a more completely fermented wine.

Third.—In what manner have the manipulations differed from those employed to produce a pure natural wine?

With the exception of the extensive use of sulphur very little can be said against the dry wines. They are almost all well fermented and matured grape juice. All the white wines but twelve have been excessively sulphured, three exceeded the limit for potassium sulphate, and four contained salicylic acid.

Two wines of the Sauterne type, Nos. 12,653 and 12,775, were excluded from the averages as evidently not representative wines, No. 12,653 gave 6.69 per cent. extract, and 3.52 per cent. reducing sugar, while No. 12,775 gave 5.48 per cent. extract. The glycerol was respectively 0.432 and 0.456 per cent. They were evidently incompletely fermented wines.

No. 12,792, a dry white wine, proved an interesting sample. It furnished the following figures: Alcohol by weight, 9.53 per cent., extract, 1.1 per cent., glycerol, 0.321 per cent., ash, 0.191 per cent., ash extract ratio, 17.36 per cent., extract-rest, 0.56 per cent. There is no doubt in my mind that this is merely an artistic mixture that never saw a vineyard but had its birth in the cellar of some wine mixer.

Another sample, No. 12,684, a miscellaneous red wine, gave only 0.105 per cent. total acid. The manufacturer here, no doubt, has used chaptalization to reduce the acidity and succeeded beyond his expectation.

Cane sugar is undoubtedly used by many to sweeten their wines, as is shown by the increased laevo rotation after inversion.

On the whole, it is evident that the California dry wines are fully equal to the European wines, and the red wines are in every respect superior to the young French Clarets. The sweet wines are to be unconditionally preferred to the European southern wines containing the same amount of alcohol and extract, and not being plastered. Their superiority is already being appreciated in Europe, and it is only a question of time when an extensive foreign market will be open to this, one of our most promising home products.

THE INFLUENCE OF COMMERCIAL GLUCOSE ON THE
POLARIZATION AFTER FERMENTATION.

To determine this point, a number of fermentations were made with mixtures of solutions of sucrose and glucose of varying strength, the same method being used as was employed in the analytical work. The results were not as uniform as desirable, probably on account of unequal rate of fermentation. They showed, however, that the amount of sucrose which is apt to be present in a wine is completely fermented in two days, so that any dextro rotation observed after that time must be due to the presence of glucose or its non-fermentable constituents.

TABLE OF RESULTS OF EXPERIMENTS MADE TO DETERMINE THE EFFECT
COMMERCIAL GLUCOSE HAS ON THE POLARIZATION
AFTER FERMENTATION.

| Original polari-
zation of
sucrose. | Original polari-
zation of
glucose. | Polarization
after two
days. | Polarization
after four
days. |
|---|---|------------------------------------|-------------------------------------|
| + 37.80 | | 0 | 0 |
| + 18.90 | | 0 | 0 |
| + 9.45 | | 0 | 0 |
| | + 16.33 | + 4.5 | + 5.0 |
| | + 16.33 | + 4.8 | + 3.8 |
| | + 9.80 | + 2.0 | + 1.8 |
| | + 9.80 | + 2.5 | + 1.8 |
| | + 3.27 | + 0.4 | 0 |
| | + 3.27 | + 1.0 | 0 |
| + 19.23 | + 16.33 | + 4.6 | + 2.8 |
| + 19.23 | + 16.33 | + 3.5 | + 3.3 |
| + 11.54 | + 16.33 | + 3.5 | + 2.3 |
| + 11.54 | + 16.33 | + 3.0 | + 2.3 |
| + 3.85 | + 16.33 | + 3.7 | + 2.4 |
| + 3.85 | + 16.33 | + 3.6 | + 3.9 |
| + 19.23 | + 9.80 | + 2.0 | + 1.7 |
| + 19.23 | + 9.80 | + 2.8 | + 2.1 |
| + 19.23 | + 3.27 | + 0.7 | + 0.9 |
| + 19.23 | + 3.27 | + 0.7 | + 0.5 |
| + 11.54 | + 9.80 | + 2.4 | + 1.0 |
| + 11.54 | + 9.80 | + 2.3 | + 1.0 |
| + 3.85 | + 9.80 | + 0.9 | + 0.3 |
| + 3.85 | + 9.80 | + 0.8 | + 0.3 |

CONTRACTION OF AQUEOUS SOLUTIONS OF ACETONE.

By K. T. P. Mc ELROY.

IN the following determinations, mixtures of known weights of acetone and water were made, the specific gravity determined by a piknometer and from this figure the volume calculated. The acetone used was bought from a New York firm and was of good purity, being free from methyl alcohol. It was fractionated and the fraction retained was boiled over calcium chlorid under a reflux condenser for three days. This portion was once more fractionated. The portion finally used boiled at 56.4° (air). Other samples were prepared for comparison by distilling acetates and by purifying the New York article by means of the sulphite compound. These various preparations possessed essentially the same boiling points and specific gravity.

In detail the method employed was to weigh a flask, add water, weigh, add acetone, reweigh, mix the united fluids by shaking and finally determine the specific gravity, first at 20° and then without refilling the piknometer, at 25°. The figures thus obtained are given in the annexed table:

TABLE I.

| Weight
acetone.
Grams. | Weight
water.
Grams. | Acetone.
Per cent. | Water.
Per cent. | Total
weight.
Grams. | Specific
gravity
20°. | Specific
gravity
25°. |
|------------------------------|----------------------------|-----------------------|---------------------|----------------------------|-----------------------------|-----------------------------|
| 39.7256 | 2.0878 | 95.01 | 4.99 | 41.8134 | 0.80717 | 0.80174 |
| 37.4627 | 4.1328 | 90.09 | 9.91 | 41.5955 | 0.82172 | 0.81626 |
| 33.4936 | 4.6211 | 87.88 | 12.12 | 38.1147 | 0.82784 | 0.82278 |
| 32.3374 | 8.0688 | 80.04 | 19.96 | 40.4062 | 0.84972 | 0.84443 |
| 30.1632 | 10.0480 | 75.02 | 24.98 | 40.2112 | 0.86342 | 0.85796 |
| 28.1373 | 12.0375 | 70.04 | 29.96 | 40.1748 | 0.87495 | 0.87051 |
| 24.2140 | 16.1070 | 60.06 | 39.94 | 40.3210 | 0.89920 | 0.89469 |
| 20.1621 | 20.0854 | 50.10 | 49.90 | 40.2475 | 0.92078 | 0.91656 |
| 16.1438 | 24.1902 | 40.03 | 59.97 | 40.3360 | 0.94057 | 0.93695 |
| 12.5495 | 28.1583 | 30.83 | 69.17 | 40.7078 | 0.95606 | 0.95286 |
| 8.0333 | 32.8027 | 19.67 | 80.33 | 40.8360 | 0.97270 | 0.97024 |
| 4.0120 | 36.0740 | 10.01 | 89.99 | 40.0860 | 0.98507 | 0.98337 |

In table II these weights are recalculated into volumes at 20° and the per cent. of contraction for that temperature calculated. The figures representing the weights of the acetone were divided by the specific gravity of acetone at 20° (0.79197) and the volume

occupied at that temperature thus found. The same operation performed on the weight of the water, using the figure 0.99826, gave the volume of that liquid. These two volumes added together gave the figures recorded in the fifth column under "sum". The weight of the mixed acetone and water divided by the specific gravity at 20° gave the actual volume occupied by the mixture at that temperature. The difference between this figure and that representing the sum of the volumes of the unmixed liquids, when divided by the latter figure gave the "Per cent. of Contraction," the figure recorded in the last column.

TABLE II. VOLUME AT 20°.

| Acetone.
Per cent. | Water.
Per cent. | Acetone.
Cubic
centimeter. | Water.
Cubic
centimeter. | Sum.
Cubic
centimeter. | Actual
volume. | Contraction.
Per cent. |
|-----------------------|---------------------|----------------------------------|--------------------------------|------------------------------|-------------------|---------------------------|
| 95.01 | 4.99 | 50.161 | 2.091 | 52.252 | 51.802 | 0.861 |
| 90.09 | 9.91 | 47.303 | 4.140 | 51.443 | 50.620 | 1.600 |
| 87.88 | 12.12 | 42.291 | 4.629 | 46.920 | 46.041 | 1.873 |
| 80.04 | 19.96 | 40.831 | 8.083 | 48.914 | 47.552 | 2.784 |
| 75.02 | 24.98 | 38.086 | 10.065 | 48.151 | 46.572 | 3.279 |
| 70.04 | 29.96 | 35.528 | 12.058 | 47.586 | 45.919 | 3.503 |
| 60.06 | 39.94 | 30.574 | 16.135 | 46.709 | 44.840 | 4.002 |
| 50.10 | 49.90 | 25.458 | 20.120 | 45.578 | 43.710 | 4.089 |
| 40.03 | 59.97 | 20.384 | 24.232 | 44.616 | 42.885 | 3.880 |
| 30.83 | 69.17 | 15.845 | 28.207 | 44.052 | 42.579 | 3.344 |
| 19.67 | 80.33 | 10.143 | 32.860 | 43.003 | 41.982 | 2.374 |
| 10.01 | 89.99 | 5.066 | 36.137 | 41.203 | 40.694 | 1.236 |

The weights, recalculated in the same way but using the specific gravities of water and acetone at 25°, which are respectively 0.78630 and 0.99712, are recorded in the following table:

TABLE III. VOLUME AT 25°.

| Acetone.
Per cent. | Water.
Per cent. | Acetone.
Cubic
centimeter. | Water.
Cubic
centimeter. | Sum.
Cubic
centimeter. | Actual
volume. | Contraction.
Per cent. |
|-----------------------|---------------------|----------------------------------|--------------------------------|------------------------------|-------------------|---------------------------|
| 95.01 | 4.99 | 50.522 | 2.094 | 52.616 | 52.153 | 0.880 |
| 90.09 | 9.91 | 47.644 | 4.144 | 51.788 | 50.958 | 1.603 |
| 87.88 | 12.12 | 42.596 | 4.634 | 47.230 | 46.324 | 1.918 |
| 80.04 | 19.96 | 41.126 | 8.092 | 49.210 | 47.850 | 2.779 |
| 75.02 | 24.98 | 38.361 | 10.077 | 48.430 | 46.858 | 3.241 |
| 70.04 | 29.96 | 35.784 | 12.072 | 47.856 | 46.151 | 3.561 |
| 60.06 | 39.94 | 30.795 | 16.153 | 46.948 | 45.067 | 4.006 |
| 50.10 | 49.90 | 25.642 | 20.143 | 45.785 | 43.911 | 4.093 |
| 40.03 | 59.97 | 20.531 | 24.260 | 44.791 | 43.050 | 3.889 |
| 30.83 | 69.17 | 15.960 | 28.240 | 44.200 | 42.722 | 3.344 |
| 19.67 | 80.33 | 10.217 | 32.897 | 43.114 | 42.090 | 2.374 |
| 10.01 | 89.99 | 5.102 | 36.180 | 41.282 | 40.764 | 1.255 |

620 CONTRACTION OF AQUEOUS SOLUTIONS OF ACETONE.

Taking the figures in Tables II and III and calculating the contractions for every five per cent. by simple interpolation the following table is obtained:

TABLE IV.

| Water. | Acetone. | Contraction at 20°. | Contraction at 25°. | Water. | Acetone. | Contraction at 20°. | Contraction at 25°. |
|--------|----------|---------------------|---------------------|--------|----------|---------------------|---------------------|
| 0.00 | 100.00 | 0.000 | 0.000 | 49.90 | 50.10 | 4.089 | 4.093 |
| 4.99 | 95.01 | 0.861 | 0.880 | 50.00 | 50.00 | 4.087 | 4.091 |
| 5.00 | 95.00 | 0.863 | 0.882 | 55.00 | 45.00 | 3.983 | 3.987 |
| 9.91 | 90.09 | 1.600 | 1.603 | 59.97 | 40.03 | 3.880 | 3.889 |
| 10.00 | 90.00 | 1.611 | 1.616 | 60.00 | 40.00 | 3.876 | 3.887 |
| 12.12 | 87.88 | 1.873 | 1.918 | 65.00 | 35.00 | 3.589 | 3.632 |
| 15.00 | 85.00 | 2.208 | 2.234 | 69.17 | 30.83 | 3.334 | 3.334 |
| 19.96 | 80.04 | 2.784 | 2.779 | 70.00 | 30.00 | 3.272 | 3.272 |
| 20.00 | 80.00 | 2.789 | 2.783 | 75.00 | 25.00 | 2.838 | 2.837 |
| 24.98 | 75.02 | 3.279 | 3.241 | 80.00 | 20.00 | 2.403 | 2.403 |
| 25.00 | 75.00 | 3.280 | 3.242 | 80.33 | 19.67 | 2.374 | 2.374 |
| 29.96 | 70.04 | 3.503 | 3.561 | 85.00 | 15.00 | 1.824 | 1.833 |
| 30.00 | 70.00 | 3.505 | 3.563 | 89.99 | 10.01 | 1.236 | 1.255 |
| 35.00 | 65.00 | 3.753 | 3.787 | 90.00 | 10.00 | 1.235 | 1.254 |
| 39.94 | 60.06 | 4.002 | 4.006 | 95.00 | 5.00 | 0.619 | 0.627 |
| 40.00 | 60.00 | 4.003 | 4.007 | 100.00 | 0.00 | 0.000 | 0.000 |
| 45.00 | 55.00 | 4.046 | 4.050 | | | | |

It was originally intended to make a determination for every five per cent. increase in the amount of acetone in the mixtures, but owing to an accident, a portion of the purified acetone was lost and from seventy per cent. acetone down, the determinations were made for each ten per cent. It will be noticed by an inspection of the table that the two series of figures, those for 20° and those for 25°, do not vary materially from each other, showing that between these temperatures the contractions of mixtures of the two liquids are practically the same. The contraction appears to reach its maximum where the weights of acetone and water employed are equal, but there is no great difference between a forty per cent. mixture and one with sixty.

ON THE HYDRATION OF CALCIUM BROMIDE AND IODIDE.¹

BY CHARLES O. CURTMAN.

Received July 16, 1894.

THE official calcium bromide of the U. S. P. is intended to be substantially anhydrous, and to contain 99.7 per cent. of pure calcium bromide. Such a salt may be obtained by saturating a solution of hydrobromic acid with pure calcium carbonate, filtering, and evaporating the solution to dryness at a temperature considerably below a red heat (about 360° C.). A solid salt may at first be obtained, containing considerable water, which melts at about 80°–81° C., and in composition closely approximates the formula $\text{CaBr}_2 + 3\text{H}_2\text{O}$. This fused salt continues to lose a small amount of water, even a few degrees above that temperature, so that it is difficult to obtain a fused salt of a definite composition.

When the heat is raised to about 180°–181° C. a greater activity appears to take place in the separation of water, and if the fused mass be cooled at that point, a salt is obtained whose formula would somewhat approximate $2\text{CaBr}_2 + 5\text{H}_2\text{O}$. At a higher temperature the water separates with a kind of effervescence, leaving a spongy, anhydrous mass.

It appears to be probable that a hydration corresponding to $\text{CaBr}_2 + 3\text{H}_2\text{O}$ exists, and may be obtained by very careful fusion at 80° C., while the intermediate one, at about 180° C., may be a mere coincidence, though closely approached by two of the commercial specimens examined.

A similar behavior was observed with *calcium iodide*, made by saturation of hydriodic acid with calcium carbonate. The salt, which fuses below the temperature of boiling water, closely approaches the formula $\text{CaI}_2 + 3\text{H}_2\text{O}$, but cannot well be isolated by fusion, on account of a gradual loss of water, even below 100° C. With a rising temperature the water escapes very slowly and gradually, and towards the end with a slight effervescence, leaving a spongy, anhydrous mass. There was no

¹ Report of Research Committee B. No. 4.

appearance of any definite intermediate stage of hydration, as was observed with the bromide.

Six specimens of calcium bromide, manufactured by different firms, were obtained in the market. They all contain water, but by no means in uniform proportions, and but little calcium bromide can be found which conforms to the directions of the U. S. P. for anhydrous salt. The following is a short résumé of the analysis of the six specimens:

No. 1. (M.)—Dry white powder. When 1.9109 grams were heated for half an hour to 80° C., neither fusion nor loss of weight occurred. When heated till the preparation became spongy and anhydrous, it lost 0.3250 gram, corresponding to 17.007 per cent. of water, and 82.993 per cent. of calcium bromide. When titrated with silver nitrate and potassium chromate as indicator, it showed 82.98 per cent. of calcium bromide.

No. 2. (M. "Dry.")—Dry white powder. 1.032 grams were heated to 86° C. without loss of weight or fusion. When heated to perfect dryness the loss was 0.164 gram = 15.9 per cent. of water, and 84.1 per cent. of calcium bromide. Titration with silver nitrate yielded eighty-four per cent. of calcium bromide.

No. 3. (M. C. W.)—White granules, which melt between 80° and 81° C. When heated to 86° C. for half an hour one gram lost 0.0032 gram = 0.32 per cent. of moisture. When heated to perfect dryness, one gram lost 0.1816 gram = 18.16 per cent. of water and 81.84 per cent. of calcium bromide. In titration with silver nitrate, 0.44 gram of the salt required 36.1 cc. of decinormal silver nitrate = 81.81 per cent. of calcium bromide.

This closely approaches the proportion of $2\text{CaBr}_2 + 5\text{H}_2\text{O}$, which requires 18.34 per cent. of water and 81.66 per cent. of calcium bromide.

No. 4. (R.)—White semi-fused lumps which melt between 80° and 81° C. When heated to dryness, 1.1036 grams lost 0.2349 gram, corresponding to 21.28 per cent. of water and 78.72 per cent. of dry substance. In titration, 0.2493 gram required 19.65 cc. of decinormal silver nitrate, corresponding to 78.6 per cent. of calcium bromide. The composition closely approaches the formula $\text{CaBr}_2 + 3\text{H}_2\text{O}$, requiring 21.27 per cent. of water.

No. 5. (P.)—White granules, melting below 100° C. 0.702

gram heated to dryness lost 0.1325 gram = 18.88 per cent. of water, and 81.12 per cent. of dry substance. Titration showed eighty-one per cent. of calcium bromide. (An approximation to the formula $2\text{CaBr}_2 + 5\text{H}_2\text{O}$, requiring 18.34 per cent. of water.)

No. 6. (P. W.)—White granules and semi-fused lumps. 1.32 grams heated to dryness lost 0.2323 gram = 17.6 per cent. of water, and 82.4 per cent. of dry substance. Titration showed eighty-two per cent. of calcium bromide.

A series of analyses of commercial specimens of calcium iodide gave similar results. The hydration in most cases made a close approach to the formula $\text{CaI}_2 + 3\text{H}_2\text{O}$, which requires 84.465 per cent. of calcium iodide, and 15.535 per cent. of water. No preparation came into my hands showing an intermediate hydration between three molecules of water and the anhydrous state.

The result of the examination is summarized as follows:

No. 1. (M. C. W.)—White, fused lumps. Contain 84.29 per cent. of calcium iodide, and 15.71 per cent. of water.

No. 2. (M.)—Yellowish-brown granules. Contain 83.92 per cent. of calcium iodide, and 16.08 per cent. of water.

No. 3. (R.)—White fused mass. Contains 84.1 per cent. of calcium iodide, and 15.9 per cent. of water.

No. 4. (P.)—Yellowish-brown granules. Contain 85.37 per cent. of calcium iodide, and 14.63 per cent. of water.

No. 5. (P. W.)—White, fused lumps. Contain 84.3 per cent. of calcium iodide, and 15.7 per cent. of water.

Specimens 1, 3, and 5, show a trace of nitrate.

From the foregoing it is very probable that a definite hydrate of calcium iodide exists, having three molecules of water, for the deviations from such a formula in all of the commercial specimens examined are not very large.

To reach more conclusive evidence it would be necessary to obtain the salt in definite crystals. Hence, solutions of calcium bromide and calcium iodide were made in water saturated at a temperature of 80° C., also in alcohol of various degrees of dilution (for a high per cent. alcohol would most likely furnish an anhydrous product). The temperature of the atmosphere being high (30°–36° C.) artificial refrigeration had to be resorted to.

The result was rather disappointing. The alcoholic solutions remained clear for many hours. From the aqueous solutions crystals of both bromide and iodide were obtained, but of such small size that it was difficult to make out their forms. Those of the iodide were slightly larger and less deliquescent and under the microscope showed rhombic needles and prisms, somewhat rounded, so as to resemble some forms of uric acid.

But they were so difficult to separate from the solution without adhering liquid, that weighing could only be approximate, and most likely would include some liquid as well as the dry substance.

The bromide, on titration, yielded 62.3 per cent. of calcium bromide, which would approximate the formula $\text{CaBr}_2 + 6\text{H}_2\text{O}$, which requires 64.92 per cent. of calcium bromide, and 35.08 per cent. of water.

The iodide yielded 69.9 per cent. of calcium iodide; the formula $\text{CaI}_2 + 6\text{H}_2\text{O}$ would demand 73.11 per cent.

In both salts the adhering liquid would render the result somewhat uncertain, and the yield of dry substance too low.

The evidence thus far is certainly not sufficient to draw definite conclusions, but I believe that the existence of hydrates of the formula $\text{CaBr}_2 + 6\text{H}_2\text{O}$ and $\text{CaBr}_2 + 3\text{H}_2\text{O}$, as well as of the corresponding hydrates of calcium iodide, is very probable.

July 8, 1894.

A STUDY OF THE CHEMICAL BEHAVIOR OF ARSENOPYRITE.

BY THOMAS MONTGOMERY LIGHTFOOT.

Received June 23, 1894.

THE variation in the weathering of pyrite, marcasite, and pyrrhotite, so often to be observed in nature, has already furnished material for several papers on the subject. The consideration of these differences in behavior leads to the question involving the chemical difference between these and allied mineral species. The effect of the electric current on these naturally occurring sulphides and sulpharsenides has already been investigated in this laboratory, but, so far as I am aware, no series of experiments with various oxidants has been recorded. Investigations as to the effect of potassium permanganate on

pyrite,¹ marcasite,¹ and pyrrhotite have been in progress during the period occupied by the experiments described in this paper. At the suggestion, therefore, of Prof. Edgar F. Smith, I undertook the study of arsenopyrite in several directions with the results that follow.

The material used in this investigation was obtained from the dump of an abandoned mine in Maine and was purchased from a dealer. The mineral was associated with quartz, with apparently no other impurity so far as the mass was concerned. To separate this quartz the mass was crushed until it passed through a twenty-four mesh screen; it was then subjected to a rising stream of water in a U tube which floated off the quartz and mixed grains. The material remaining in the tube was found to be entirely free from quartz. The pure material was then washed with distilled water, spread on a filter paper, and dried at a gentle heat. A magnet was used to remove any particles of iron that might have entered the material from the crusher. This purified arsenopyrite was then preserved in a glass-stoppered bottle, and portions of it ground from time to time as required in an agate mortar. An estimation of the total sulphur contained in this arsenopyrite gave as the average of three determinations 19.77 per cent., almost the theoretical for the ratio of FeS_2 to FeAs_2 , as 1 : 1.

Action of Potassium Permanganate at the Ordinary Temperature.—The first series of experiments consisted in determining the effect of potassium permanganate solutions of varying strengths on the mineral, the oxidant being allowed to act for varying periods of time and at 100° as well as at the ordinary temperature (21° – 22°). The method of procedure at the ordinary temperature was the same in each case, and was as follows: Two-tenths of a gram of the finely ground mineral were introduced into a glass-stoppered bottle and fifty cc. of the permanganate solution added. The bottle and its contents were then shaken at frequent intervals to prevent the caking of the mineral against the walls of the vessel and to expose fresh surfaces to the action of the permanganate. Four strengths of solution were employed, $\frac{1}{100}$ normal, one per cent., three per cent., and five

¹ See "A Comparative Study of the Chemical Behavior of Pyrite and Marcasite," by A. P. Brown. *Proc. Amer. Philos. Soc.*, 1894.

per cent., and each was allowed to act for periods of one, two, three, four, and five hours. Duplicate trials were made in each case. After the solution had been in contact with the mineral for the specified time the contents of the bottle were thrown on a filter, the residue was washed on the filter and rejected, and the filtrate was acidified with hydrochloric acid and the sulphur oxidized, and determined as barium sulphate. In this determination trouble was experienced in obtaining complete precipitation of the sulphuric acid, even after long digestion and standing, and this may account in part for the great irregularities shown in the results of these oxidations. It should be noted that the four-hour experiments (which show notable irregularities) were performed after the completion of the rest of the series, but presumably under the same conditions.

The results of this series of oxidations are tabulated below. It will be noticed that the two results given in each case sometimes correspond closely with each other and at other times one is more than double the other. There is no reason why these results should vary in this way so far as external conditions are concerned as these duplicates were in each case made at the same time and under the same conditions. The average of the two in a number of cases would seem to be nearer the expected result. Omitting consideration of the four-hour trials, reference to which has already been made, it is seen that in each case the oxidation is practically completed at the end of the first hour, and is comparatively slight after all. The mineral is not nearly so readily affected by this oxidant as the simple iron sulphides.

(1) TABLE SHOWING THE AMOUNT OF SULPHUR OXIDIZED IN ARSENO-PYRITE BY POTASSIUM PERMANGANATE AT THE ORDINARY TEMPERATURE.

| Strength of permanganate solution. | One hour. | | Two hours. | | Three hours. | | Four hours. | | Five hours. | |
|------------------------------------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|
| | Sulphur oxidized. Per cent. | Average. Per cent. | Sulphur oxidized. Per cent. | Average. Per cent. | Sulphur oxidized. Per cent. | Average. Per cent. | Sulphur oxidized. Per cent. | Average. Per cent. | Sulphur oxidized. Per cent. | Average. Per cent. |
| 100 normal.. | 0.34 | | 0.34 | | 0.33 | | 0.53 | | 0.52 | |
| | 0.33 | 0.33 | 0.34 | 0.34 | 0.49 | 0.41 | 0.51 | 0.52 | 0.27 | 0.36 |
| 1 per cent... | 0.25 | | 0.31 | | 0.38 | | 0.73 | | 0.25 | |
| | 0.58 | 0.42 | 0.24 | 0.28 | 0.40 | 0.39 | 0.75 | 0.74 | 0.46 | 0.35 |
| 3 per cent... | 0.61 | | 0.43 | | 0.40 | | 1.20 | | 0.55 | |
| | 0.52 | 0.56 | 0.28 | 0.36 | 0.38 | 0.39 | 1.40 | 1.30 | 0.44 | 0.50 |
| 5 per cent... | 0.41 | | 0.27 | | 0.34 | | 0.25 | | 0.59 | |
| | 0.16 | 0.29 | 0.75 | 0.51 | 0.69 | 0.52 | 0.63 | 0.44 | 0.33 | 0.48 |

Action of Potassium Permanganate at 100°.—In conducting experiments at 100° the bottles containing the mineral and permanganate solution were suspended in boiling water, which covered about one-half of the bottle, and the stoppers introduced after the contents of the bottle had reached the temperature of the water. The other details of these experiments were the same as for those conducted at the ordinary temperature. The action in this case was considerably more energetic, and the results obtained were much more concordant. The best results in this case were with the $\frac{1}{100}$ normal solution which are remarkably close in duplicate and the averages show a regular rise in the amount of sulphur oxidized in proportion to the time of oxidation. The one per cent. solution gave discordant results, but curiously the averages show a fairly regular rate of oxidation. The three and five per cent. solutions give concordant results in duplicate and show on the other hand an approach to the character of oxidation shown at the ordinary temperature, but several times greater in degree. The oxidation for each of the three and five per cent. solutions seems to be nearly complete at the end of the first hour, the rate of oxidation thereafter being very slow.

The results of this series of experiments are given in the following table, along with their averages:

(2) TABLE SHOWING THE AMOUNT OF SULPHUR OXIDIZED IN ARSENOPYRITE BY POTASSIUM PERMANGANATE AT 100°.

| Strength of permanganate solution. | One hour. | | Two hours. | | Three hours. | | Four hours. | | Five hours. | |
|------------------------------------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|
| | Sulphur oxidized. Per cent. | Average. Per cent. | Sulphur oxidized. Per cent. | Average. Per cent. | Sulphur oxidized. Per cent. | Average. Per cent. | Sulphur oxidized. Per cent. | Average. Per cent. | Sulphur oxidized. Per cent. | Average. Per cent. |
| $\frac{1}{100}$ normal.. | 0.60 | 0.59 | 0.82 | 0.77 | 1.05 | 1.05 | 1.09 | 1.19 | 1.28 | 1.29 |
| | 0.57 | | 0.71 | | 1.06 | | 1.30 | | 1.31 | |
| 1 per cent... | 1.06 | 0.67 | 1.44 | 1.13 | 2.27 | 1.25 | 1.25 | 1.27 | 1.46 | 0.85 |
| | 0.29 | | 0.83 | | 0.24 | | 1.28 | | 0.25 | |
| 3 per cent... | 1.45 | 1.31 | 1.36 | 1.26 | 1.61 | 1.53 | 1.56 | 1.57 | 1.24 | 1.59 |
| | 1.18 | | 1.16 | | 1.45 | | 1.59 | | 1.95 | |
| 5 per cent... | 1.12 | 1.40 | 1.25 | 1.33 | 1.36 | 1.41 | 1.74 | 1.77 | 1.70 | 1.73 |
| | 1.68 | | 1.40 | | 1.46 | | 1.80 | | 1.75 | |

The foregoing results will be more significant if compared with the results of similar experiments made with related minerals. As already noted, experiments on the chemical behavior of pyrite

and marcasite have been conducted in this laboratory recently, and from the average results of the action of potassium permanganate on the above two minerals I have been enabled to compile a comparative table in which they are compared with my results on arsenopyrite. In order to compare the action of the permanganate on the sulphur of these three minerals on equal terms, I have calculated from Brown's tabulated results of average amounts oxidized the percentage of the contained sulphur oxidized, and doing the same for my averages on arsenopyrite have combined these calculated percentages in a table in which the action of varying strengths of solution for varying times on the three minerals can be seen at a glance.

(3) TABLE SHOWING PERCENTAGE OF THE CONTAINED SULPHUR OXIDIZED BY POTASSIUM PERMANGANATE IN ARSENOPYRITE (A),¹ PYRITE (P),² AND MARCASITE (M).²

| | | Strength of Permanganate Solution. | | | | | | | |
|--------------|---|------------------------------------|-----------------------------|-------------------------------|------------------------------|-------------------------|------------------------------|--------------------------------|-------------------------------|
| | | 100
normal.
22°. | One
per
cent.
22°. | Three
per
cent.
22°. | Five
per
cent.
22°. | 100
normal.
100°. | One
per
cent.
100°. | Three
per
cent.
100°. | Five
per
cent.
100°. |
| One hour... | A | 1.69 | 2.12 | 2.75 | 1.45 | 2.98 | 3.44 | 6.66 | 7.11 |
| | P | 1.46 | 3.20 | 4.78 | 5.19 | 7.59 | 11.31 | 11.74 | 14.91 |
| | M | 2.01 | 2.29 | 5.25 | 4.33 | 5.94 | 12.06 | 12.13 | 15.52 |
| Two hours.. | A | 1.73 | 1.41 | 1.83 | 2.61 | 3.89 | 5.74 | 6.14 | 6.74 |
| | P | 2.19 | 2.68 | 4.26 | 5.79 | 8.85 | 13.09 | 12.81 | 14.10 |
| | M | 3.48 | 2.27 | 4.18 | 6.39 | 7.20 | 11.12 | 14.94 | 15.52 |
| Three hours. | A | 2.03 | 2.01 | 1.98 | 2.24 | 5.32 | 6.37 | 7.77 | 7.14 |
| | P | 2.59 | 3.49 | 5.25 | 5.19 | 6.29 | 15.71 | 12.77 | 18.47 |
| | M | 3.82 | 3.86 | 5.38 | 6.18 | 7.04 | 16.05 | 17.66 | 24.88 |
| Four hours. | A | 2.66 | 3.74 | 6.58 | 2.24 | 6.04 | 6.43 | 8.00 | 8.88 |
| | P | 3.26 | 3.46 | 4.78 | 5.42 | (3.82) | 11.46 | 20.12 | 22.24 |
| | M | (2.34) | 4.35 | 5.40 | 5.92 | 10.56 | 13.87 | 18.37 | 27.84 |
| Five hours.. | A | 2.01 | 1.81 | 2.52 | 2.36 | 6.61 | 4.33 | 8.08 | 8.76 |
| | P | 3.22 | 3.37 | 4.78 | 5.66 | 10.57 | 12.90 | 20.77 | 28.09 |
| | M | 4.46 | 4.20 | 5.25 | 7.08 | 10.51 | 17.06 | (14.16) | 30.67 |

From the above table a plat has been made to show the rates of oxidation of sulphur in arsenopyrite by different strengths of potassium permanganate solutions acting for different times, the results obtained by each strength of solution being combined into a continuous curve (Plate I). The points already mentioned above as to the action of different strengths of solution

¹ Calculated from averages as given in Tables (1) and (2).

² Calculated from average results as given by Brown in "A Comparative Study of the Chemical Behavior of Pyrite and Marcasite." *Proc. Amer. Philos. Soc.*, 1894.

are here graphically shown. A large value has been given the vertical component (percentage oxidized) in order to separate the curves more fully.

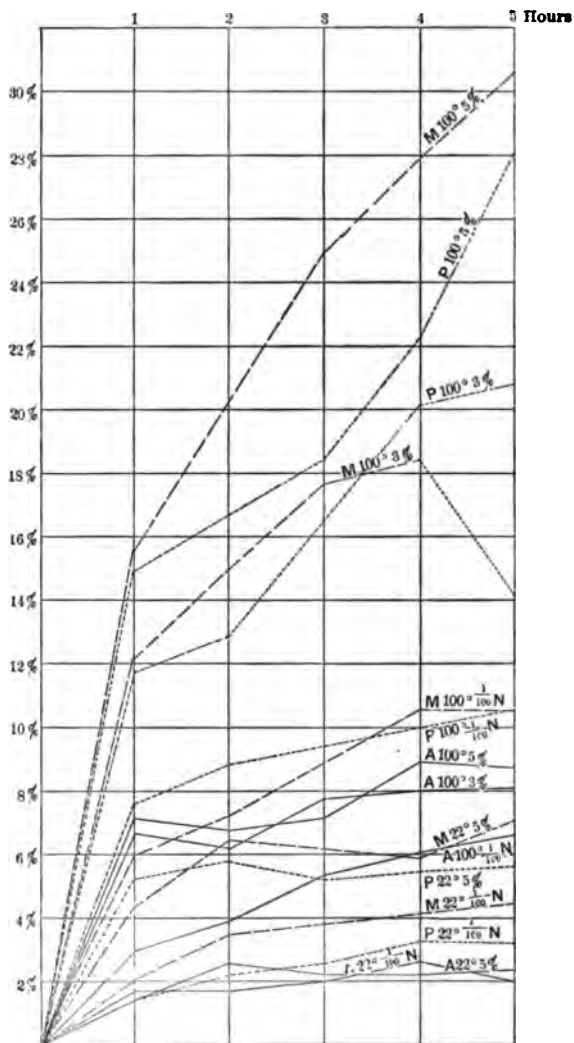


PLATE I.

A comparative plot is also given (Plate II) of selected results from table (3) in which only those curves for arsenopyrite are

selected which present a reasonable degree of regularity. They are not, however, necessarily the best in the pyrite-marcasite series.

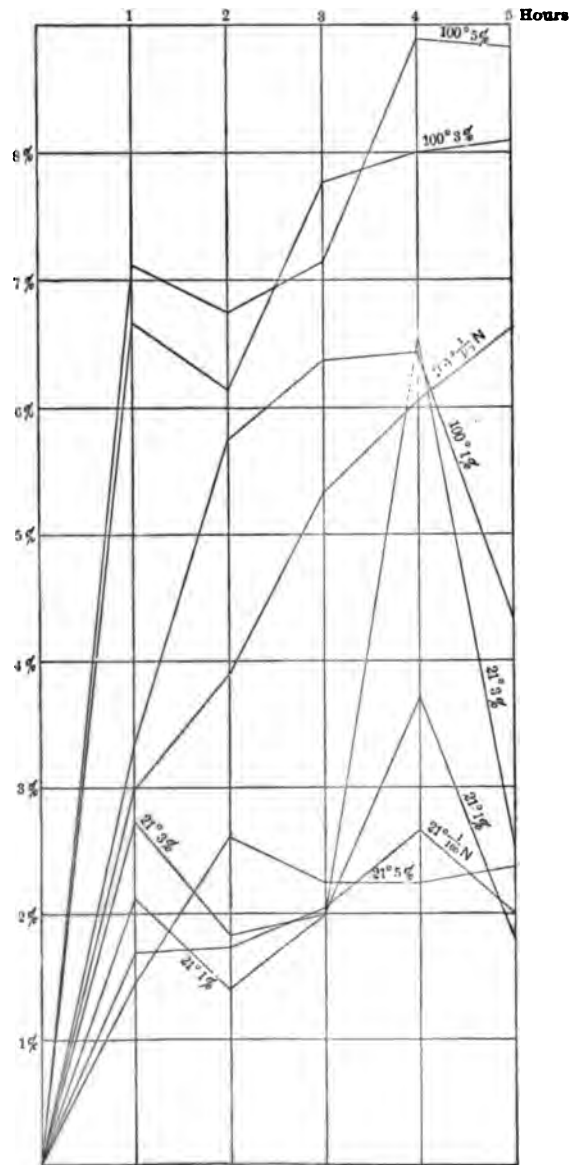


PLATE 2.

A smaller value is here given to the vertical component than in the last case in order that the pyrite and marcasite curves may be platted in full, as they rise so much higher than the arsenopyrite curves. It would be natural to suppose that the curves of arsenopyrite would be more comparable to those of marcasite than to those of pyrite on account of the isomorphism shown by their crystals, and an inspection of the platted curves will show that this is in general, correct. Take for instance the curves showing the action of $\frac{1}{100}$ normal solution of permanganate at ordinary temperature (marked A, 22° , $\frac{1}{100}$ N, etc.); it is seen that at two, three, and five hours the per cent. of oxidation of the contained sulphur in marcasite is almost exactly double that for arsenopyrite. The same condition of affairs is seen on comparing the $\frac{1}{100}$ normal solutions at 100° . It has already been noted that with the more concentrated solutions of permanganate at 100° the greater part of the oxidation of the arsenopyrite has taken place at the end of the first hour, but in the case of the pyrite and marcasite this is not the case. Their curves of oxidation rise rapidly for the three per cent. and five per cent. solutions, and are hence not comparable to those of arsenopyrite. The entire results given in table (3) are not platted here as they would simply confuse those already shown, but those obtained in the cold would serve to further illustrate the comparison that has been made between arsenopyrite and marcasite. The fact above illustrated that the sulphur in marcasite oxidizes twice as rapidly as that in arsenopyrite is what we might expect from the formula of the two minerals, marcasite being FeS_2 , and arsenopyrite FeSAs .

Action of Hydrochloric Acid Gas on Arsenopyrite at Elevated Temperatures.—Experiments on the removal of sulphur from arsenopyrite by the action of hydrochloric acid gas at elevated temperatures were tried in the following manner. Two-tenths of a gram of the finely ground mineral, weighed out in a porcelain boat were subjected to the action of a stream of dry hydrochloric acid gas for one, two, and three hours at 300° and 325° , the temperatures being graded by the melting points of various salts. The sulphur in the material remaining in the boat after the action of the hydrochloric acid was determined as barium

sulphate, and the amount lost estimated by difference. While no very large amounts of sulphur were removed in this way (except in one case) the amount of arsenic driven off in the process seemed to be considerable, a large sublimate of metallic arsenic forming in the tube, and some passing out with the stream of gas. As will be seen from the results as given in the table (4) the difference in temperature between 300° and 325° caused a marked difference in the amount of sulphur removed. The temperature called 300° was between the melting points of acid sodium sulphate, NaHSO_4 , and sodium nitrate NaNO_3 ; that called 325° was between sodium nitrate, NaNO_3 , and potassium chlorate, KClO_3 . The boats containing the mineral were heated in glass tubes so that the reaction could be watched. The amounts of sulphur removed at the lower temperature show no notable increase between the second and third hour, while those at the higher temperature show rapid increase of sulphur lost with the increase of time, perhaps indicating a critical temperature for the reaction of hydrochloric acid with the mineral. A comparison of these results with those obtained by Brown¹ for pyrite and marcasite is given in the table, the results being calculated to percentage of contained sulphur.

(4) TABLE SHOWING RELATIVE AMOUNTS OF SULPHUR REMOVED FROM ARSENOPYRITE, PYRITE AND MARCASITE BY ACTION OF DRY HYDROCHLORIC ACID GAS AT ELEVATED TEMPERATURES.

| Mineral. | One hour. | | Two hours. | | Three hours. | |
|-----------------------------------|----------------------------|--------------------------------|----------------------------|--------------------------------|----------------------------|--------------------------------|
| | Amount of sulphur removed. | Percent- age of total sulphur. | Amount of sulphur removed. | Percent- age of total sulphur. | Amount of sulphur removed. | Percent- age of total sulphur. |
| Arsenopyrite, 300° | 1.10 | 5.56 | 1.84 | 9.32 | 1.86 | 9.42 |
| Pyrite, 300° | 10.73 | 20.10 | | | | |
| Marcasite, 300° | 7.19 | 13.48 | | | | |
| Arsenopyrite, 325° | 1.62 | 8.29 | 2.82 | 14.29 | 12.21 | 61.78 |
| Pyrite, 325° | | | | | 17.13 | 32.12 |
| Marcasite, 325° | | | | | 10.70 | 20.06 |

Action of a Solution of Copper Sulphate Under Pressure on Arsenopyrite.—A single experiment on the action of copper sulphate in water solution on this mineral was tried by heating two-tenths of a gram of the finely ground mineral with a dilute solution of the salt in a sealed glass tube for six hours at a temperature approximating 200° . But little ferrous iron was found in

¹ Op. cit.

the solution, which seems to indicate that the iron present in the mineral is ferric. Some crystalline green arsenate (?) of copper was observed in the tube.

The results of the oxidation experiments detailed in this paper seem to bear out the relationship between arsenopyrite and marcasite indicated in the isomorphism of the two minerals, but the arsenic seems to be a disturbing element which fixes a limit, at an early stage of the oxidation, to further action of any given strength of the oxidant. The experiments with hydrochloric acid gas seem again to show the disturbing action of the arsenic present, which, at the higher temperature at least, is probably removed by heat alone, as is the case with the majority of diarsenides, leaving finally a compound readily acted on by the hydrochloric acid as shown by the large amount of sulphur removed in the three-hour's experiment at 325°. The results of this series of experiments are, therefore, not very significant as compared with those for pyrite and marcasite as given in Brown's paper. If, as indicated by the oxidation experiments, the arsenopyrite is rather to be compared with marcasite, in which Brown has shown that the iron is in the ferrous condition, we may look on arsenopyrite as a ferrous compound, but this conclusion seems to be negatived by the result of the single experiment of decomposing the mineral in a solution of copper sulphate under pressure. In this experiment it will be remembered, no considerable amount of ferrous iron was found. Further research in this latter direction must be made before definite statements as to the constitution of arsenopyrite can be formulated.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

THE PROTEIDS OF THE KIDNEY BEAN.¹

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

THE only work on the proteids of the kidney bean having importance at the present time, is that of Ritthausen. This investigator in 1883, stated² that the extract of the white bean

¹ Reprinted from the report for 1893 of the Connecticut Agricultural Experiment Station, New Haven.

² *J. prakt. Chem.*, 103, 204.

which has a weak alkaline reaction, and is extremely difficult to filter, when made clear by subsidence, yields on adding acetic acid, a voluminous precipitate, amounting to about eleven per cent. of the seed, having the following composition :

| | |
|----------------|--------|
| Carbon | 51.48 |
| Hydrogen | 7.04 |
| Nitrogen | 14.40 |
| Sulphur..... | 0.42 |
| Oxygen | 26.66 |
| | <hr/> |
| | 100.00 |

In 1884, Ritthausen¹ published the results of further study of this seed. He then stated that the proteid, obtained in his earlier experiments, was wholly insoluble in five per cent. sodium chloride solution, but partially dissolved in two per cent. brine, and by diluting was precipitated in a form entirely like the original substance. By treating the bean meal with alcohol he found that clarification of the extracts was greatly facilitated and he, therefore, used meal so treated in his subsequent experiments.

By extraction with two per cent. sodium chloride solution, and clearing the extract by subsidence, he obtained, in two cases, precipitates of proteid, amounting respectively to 13.2 and 11.45 per cent. of the meal. Another preparation, equal to 8.67 per cent., he obtained from an aqueous extract of the meal precipitated with hydrochloric acid, the precipitate being redissolved in potash water and the solution neutralized after filtering clear. By extracting the bean meal with dilute hydrochloric acid, he obtained 10.07 per cent. of proteid. Preparations made by precipitating aqueous solutions with hydrochloric acid and sodium chloride extracts by dilution and submitting the precipitates to analysis without re-solution and consequent purification, had a composition similar to that found for the earlier preparations.

The precipitate obtained from hydrochloric acid solutions, had a different composition, agreeing with that of the proteid extracted by dilute salt solution both from the older preparations and from the freshly formed precipitate produced by acids in the aqueous extract, as well as with that of the insoluble portion remaining after this extraction, and also with that of the

¹ *J. prakt. Chem.*, N. Folge, 29, 452.

precipitate produced by hydrochloric acid in the aqueous extract, redissolved in dilute potash water and precipitated by neutralization. An average of five quite closely agreeing analyses of the proteid thus obtained, is shown by the following figures:

| | |
|----------------|--------|
| Carbon | 52.55 |
| Hydrogen | 7.09 |
| Nitrogen | 16.18 |
| Sulphur..... | 0.43 |
| Oxygen | 23.75 |
| | <hr/> |
| | 100.00 |

This proteid, Ritthausen remarked, "is so similar in composition to albumin, that one might be led to regard it as an albumin, low, indeed, in sulphur." In most respects the experiments of the writer now to be detailed, confirm these observations of Ritthausen, but in two particulars his statements have not been corroborated. The reaction of the aqueous extract, I have found in all cases, to be distinctly acid, even when the beans were tested within two minutes after crushing. Ritthausen's statement that his earlier preparations were wholly insoluble in five per cent. solution of sodium chloride, while a very considerable quantity was dissolved by two per cent. brine, is difficult to understand, unless as implied, though not directly so expressed, the presence of the proteid was detected by largely diluting the salt-water extracts. The writer has found that strong saline solutions, unless containing a large proportion of this proteid, are not precipitated by dilution, the salt being present in sufficient quantity to serve as a solvent for the diminishing percentage of the dissolved proteid.

I have been able to identify and obtain in a state of comparative purity, two distinct proteids, one, the most abundant, having quite the properties of a globulin, which I shall designate *phaseolin* and another, not so definite in character, that may be distinguished as *phaselin*.

PREPARATION OF PHASEOLIN.

An extract was prepared by treating 500 grams of freshly ground bean meal,¹ which had been previously exhausted with ether, with one liter of two per cent. sodium chloride solution.

¹ The "White Medium Field Bean," the seeds being about $\frac{3}{8}$ inch or one cm. in length, was used for this investigation.

The residue was strained out on coarse linen squeezed dry in a screw press, and again treated with a liter of the two per cent. salt solution. The resulting extract filtered very slowly and not wholly clear; about nine-tenths of it was finally obtained as a turbid filtrate. This was saturated with ammonium sulphate and the precipitate produced collected on a filter and separated as completely as possible from the solution. This precipitate was removed from the filter and treated with water. Much of the substance went into solution, but a considerable part remained undissolved. After twenty-four hours filtration, a very nearly clear liquid was obtained, amounting to about two-thirds of the solution. This was then dialyzed in a stream of river water for six days. When thus freed from chlorides, the contents of the dialyzer were transferred to a filter, but only a part of the separated proteid remained on the paper, the filtrate being milky. The precipitate collected was washed with water, alcohol and ether, and when dried over sulphuric acid, weighed sixteen grams. This preparation had the following composition:—1.

PHASEOLIN, PREPARATION 1.

| | I. | II. | Average. | Ash-free. |
|---------------|-------|-------|----------|-----------|
| Carbon..... | 51.73 | | 51.73 | 52.23 |
| Hydrogen ... | 6.89 | | 6.89 | 6.95 |
| Nitrogen | 16.28 | 16.14 | 16.21 | 16.37 |
| Sulphur..... | 0.68 | 0.54 | 0.61 | 0.62 |
| Oxygen | | | | 23.83 |
| Ash | 0.96 | | 0.96 | |
| | | | | 100.00 |

As this preparation separated from a not perfectly clear solution, and therefore, presumably, was impure, a part of it was dissolved in one per cent. sodium chloride brine and precipitated by dilution. After standing a few hours to settle, the precipitate was filtered off and washed with distilled water, with alcohol and with ether. Its composition is as follows:—2.

PHASEOLIN, PREPARATION 2.

| | | Ash-free. |
|----------------|-------|-----------|
| Carbon | 52.35 | 52.60 |
| Hydrogen | 6.63 | 6.69 |
| Nitrogen | 16.42 | 16.56 |
| Sulphur | 0.63 | 0.63 |
| Oxygen | | 23.52 |
| Ash | 0.82 | |
| | | 100.00 |

Another preparation was made by treating the fine ground beans, previously extracted both with ether and alcohol, with ten per cent. sodium chloride solution, as long as any proteid was removed. The extract was allowed to stand over night and the very nearly clear, greenish-yellow liquid was decanted from the sediment and saturated with ammonium sulphate. The precipitated proteid was collected on a filter and dissolved in dilute salt solution. This liquid was filtered as clear as possible and then dialyzed. When freed from chlorides, the globulin which had separated was filtered off, and washed and dried in the usual manner. This preparation, 3, had the following composition:

| PHASEOLIN, PREPARATION 3. | | | | |
|---------------------------|-------|-------|---------|-----------|
| | I. | II. | Average | Ash-free. |
| Carbon..... | 52.19 | | 52.19 | 52.60 |
| Hydrogen..... | 6.67 | | 6.67 | 6.72 |
| Nitrogen..... | 16.01 | 16.06 | 16.04 | 16.17 |
| Sulphur..... | 0.63 | | 0.63 | 0.63 |
| Oxygen..... | | | | 23.88 |
| Ash..... | 0.79 | | 0.79 | |
| | | | | 100.00 |

As this preparation, 3, separated from a solution which could not be filtered perfectly clear, it is undoubtedly impure. In order to determine whether the preparations thus far obtained were mixtures of two or more globulins, the following were made by fractionally precipitating the extracts. The extraction was also carried out in such a way as to afford an approximate determination of the amount of phaseolin contained in the extracts.

One hundred grams of bean meal were treated with 500 cc. of one per cent. sodium chloride solution, strained through cloth, and allowed to stand so as to deposit most of the suspended matter. The solution was then decanted and 350 cc. of nearly clear extract obtained, being, therefore, approximately seven-tenths of the whole. This solution was then diluted with 1,050 cc. of distilled water and allowed to stand until the precipitate so produced had settled. The latter was collected on a filter, washed with alcohol and ether, and when air-dried was found to weigh 4.76 grams; preparation 4. The filtrate from 4 was diluted with about an equal bulk of water and carbon dioxide was

passed through it. After standing some time, a precipitate settled out, leaving the liquid nearly clear. This was decanted and the precipitate collected on a filter and treated like 4. This gave preparation 5, which weighed 3.76 grams. The filtrate from 5 was further diluted with a considerable quantity of water and carbon dioxide again passed through the solution. This gave preparation 6, weighing, air-dry, 1.12 grams. The filtrate from 6 was treated with acetic acid, and a further small precipitate, 7, obtained, weighing 0.7 gram. The four preparations together weighed 10.34 grams, and as they were obtained from seven-tenths of the total extract, were approximately equivalent to the proteid derived from seventy grams of air-dry bean meal or to 14.77 per cent. of the meal. It is evident that in preparing the globulin by dialysis in the manner just described, only a part was obtained. As preparation 4 was separated from an unfiltered extract, it was necessary to dissolve and reprecipitate it before submitting it to analysis. It was accordingly treated with one per cent. sodium chloride solution, but had become largely insoluble in brine. The insoluble matter was filtered off, the clear filtrate diluted, and carbon dioxide passed through it as long as globulin was precipitated.

The precipitate was filtered off, washed thoroughly with water, alcohol, and ether, and dried over sulphuric acid. Only one gram of proteid, preparation 4, was recovered.

PHASEOLIN, PREPARATION 4.

| | I. | II. | Average. | Ash-free. |
|----------------|-------|-------|----------|-----------|
| Nitrogen | 16.05 | 15.89 | 15.97 | 16.12 |
| Ash | 0.93 | | 0.93 | |

Analyses of the other preparations gave the following results:

PHASEOLIN, PREPARATION 5.

| | I. | II. | Average. | Ash-free. |
|----------------|-------|------|----------|-----------|
| Carbon | 52.14 | | 52.14 | 52.54 |
| Hydrogen | 6.78 | | 6.78 | 6.83 |
| Nitrogen | 16.35 | | 16.35 | 16.48 |
| Sulphur | 0.62 | 0.53 | 0.58 | 0.58 |
| Oxygen | | | | 23.57 |
| Ash | 0.77 | | 0.77 | |

100.00

PHASEOLIN, PREPARATION 6.

| | | Ash-free. |
|----------------|-------|-----------|
| Nitrogen | 15.83 | 16.23 |
| Ash | 2.51 | |

PHASEOLIN, PREPARATION 7.

| | | |
|----------------|-------|-----------|
| | | Ash-free. |
| Nitrogen | 16.70 | 16.87 |
| Ash | 1.04 | |

A larger quantity of meal was next extracted, and the extract fractionally precipitated in the following manner:

Five hundred grams of meal were treated with 1,500 cc. of one per cent. sodium chloride solution, and the extract filtered once through good filter paper. About two-thirds of the extract were thus obtained as a turbid solution. Three volumes of distilled water were added, and the large precipitate formed was designated A. Through the filtrate from A, a current of carbonic acid gas was passed, and the resulting precipitate filtered off and marked B. Precipitate A was treated with about fifty cc. of ten per cent. sodium chloride brine and filtered as well as possible. A considerable part of A had become insoluble, and the filtration was exceedingly slow. After two and one-half days, most of the solution had filtered very nearly clear. This was then diluted with about ten times its volume of water, and the precipitate thereby produced, filtered off, washed with alcohol and ether, and dried over sulphuric acid; preparation 8. The filtrate from 8 was again diluted with a large quantity of water and a second precipitate obtained in a like manner; preparation 9.

The filtrate from 9 gave a very small additional precipitate with carbon dioxide, weighing, when dry, only 0.2 gram. A portion of precipitate B was dried and marked preparation 10. Five grams of precipitate B were dissolved in one-half per cent. sodium chloride solution, previously heated to 70°, filtered hot from the considerable insoluble matter, an equal volume of water heated to 70° was added to the filtrate, and the solution very slowly cooled. The proteid separated in well-developed spheroids. When this precipitate was filtered off and washed with water, the substance began to dissolve, as the salts were washed out, in the same way as the globulins of the oat kernel, castor bean, and hemp-seed dissolve, when they are washed with water, after separating from warm salt solutions on cooling. Alcohol was then added to the contents of the funnel, and the substance washed with alcohol and ether, and dried. This preparation, 11, weighed two grams.

The insoluble proteid filtered from the solution which yielded 11, was dissolved in two-tenths per cent. potash water and after filtering, the solution was exactly neutralized with two-tenths per cent. hydrochloric acid. The precipitate, which was very readily soluble in dilute sodium chloride solution, after washing with water, alcohol and ether, and drying, weighed 0.65 gram; preparation 12.

Another portion of precipitate B weighing 3.35 grams, was treated with one-half per cent. sodium chloride brine, and heated to 70°. The insoluble matter was filtered off, washed with hot dilute salt solution, with water, alcohol and ether, and when dried formed preparation 13, weighing 1.16 gram. The dissolved proteid separated from the filtrate and washings of 13 on gradually cooling, and after washing with dilute alcohol, absolute alcohol, and ether, gave 1.54 grams of preparation 14. All were then dried at 110°, and analyzed with the following results:

PHASEOLIN, PREPARATION 8.

| | I. | II. | Average. | Ash-free. |
|---------------|-------|-------|----------|-----------|
| Carbon..... | 52.31 | | 52.31 | 52.72 |
| Hydrogen..... | 7.18 | | 7.18 | 7.24 |
| Nitrogen..... | 16.32 | 16.32 | 16.32 | 16.45 |
| Sulphur..... | 0.67 | 0.66 | 0.67 | 0.67 |
| Oxygen..... | | | | 22.92 |
| Ash..... | 0.80 | | 0.80 | |
| | | | | 100.00 |

PHASEOLIN, PREPARATION 9.

| | | | Ash-free. |
|-----------------|-------|--|-----------|
| Carbon | 51.89 | | 52.35 |
| Hydrogen | 6.83 | | 6.89 |
| Nitrogen | 16.37 | | 16.52 |
| Sulphur } | | | 24.24 |
| Oxygen } | | | |
| Ash | 0.88 | | |
| | | | 100.00 |

PHASEOLIN, PREPARATION 10.

| | I. | II. | Average. | Ash-free. |
|---------------|-------|-------|----------|-----------|
| Carbon..... | 51.89 | 51.98 | 51.94 | 52.74 |
| Hydrogen..... | 6.84 | 6.64 | 6.74 | 6.84 |
| Nitrogen..... | 16.40 | | 16.40 | 16.65 |
| Sulphur..... | 0.63 | | 0.63 | 0.64 |
| Oxygen..... | | | | 23.13 |
| Ash..... | 1.52 | | 1.52 | |
| | | | | 100.00 |

PHASEOLIN, PREPARATION 11.

| | | Ash-free. |
|-----------------|-------|--------------|
| Carbon | 52.34 | 52.49 |
| Hydrogen | 6.78 | 6.80 |
| Nitrogen | 16.80 | 16.85 |
| Sulphur } | | 23.86 |
| Oxygen } | | |
| Ash | 0.30 | |
| | | <hr/> 100.00 |

PHASEOLIN, PREPARATION 12.

| | | Ash-free. |
|----------------|-------|-----------|
| Nitrogen | 16.54 | 16.67 |
| Ash | 0.81 | |

PHASEOLIN, PREPARATION 13.

| | | Ash-free. |
|-----------------|-------|--------------|
| Carbon | 52.76 | 53.06 |
| Hydrogen | 6.81 | 6.85 |
| Nitrogen | 16.59 | 16.68 |
| Sulphur } | | 23.41 |
| Oxygen } | | |
| Ash | 0.57 | |
| | | <hr/> 100.00 |

PHASEOLIN, PREPARATION 14.

| | | Ash-free. |
|-----------------|-------|--------------|
| Carbon | 52.12 | 52.49 |
| Hydrogen | 6.68 | 6.73 |
| Nitrogen | 16.33 | 16.45 |
| Sulphur } | | 24.13 |
| Oxygen } | | |
| Ash | 0.72 | |
| | | <hr/> 100.00 |

These results show that the greater part of the proteid extracted by sodium chloride solution, consists of a single globulin, amounting at least to fifteen per cent. of the seed. The greater part of the proteid remaining in the seed after extraction with salt solution, is presumably the same globulin, possibly inclosed in the tissue of the coarsely ground seed, so that it was not reached by the salt solution, or more likely, an insoluble or "albuminate" form of this globulin, as the following experiment indicates. After complete exhaustion with ten per cent. sodium chloride brine, of the meal from which preparation 3 was obtained, the residue was extracted with two-tenths per cent.

potash water, the extract allowed to stand over night and then decanted and precipitated with hydrochloric acid, added in very slight excess. The precipitate was washed by decantation, redissolved in potash water and filtered clear. This solution was then precipitated by hydrochloric acid, and as the proteid separated imperfectly, it was treated with alcohol and ether, and filtered off. After washing with dilute alcohol, absolute alcohol and ether, it was dried and analyzed; preparation 15.

PHASEOLIN, PREPARATION 15.

| | | Ash-free. |
|-----------------|-------|-----------|
| Carbon | 51.57 | 52.47 |
| Hydrogen | 6.78 | 6.90 |
| Nitrogen | 15.71 | 16.00 |
| Sulphur } | | 24.63 |
| Oxygen } | | |
| Ash | 1.72 | |
| | | 100.00 |

Another preparation of the globulin was made by treating 100 grams of bean meal, previously extracted with ether, with 500 cc. of *distilled water*, straining through a cloth, allowing the extract to stand over night to deposit suspended matter and decanting the slightly turbid liquid, of which the 250 cc. thus obtained were diluted to 2,000 cc. and treated with a current of carbonic acid gas. On standing, the considerable precipitate settled out so that the solution could be filtered. The precipitate was washed with water, alcohol, and ether, and when dried over sulphuric acid weighed 5.5 grams. As the extract employed, measured one-half the volume of the water applied to the meal, the yield of globulin was in this case approximately eleven per cent. of the bean meal. Although precipitated from a somewhat turbid solution, and consequently not quite pure, this preparation was analyzed with the following results:

PHASEOLIN, PREPARATION 16.

| | I. | II. | Average. | Ash-free. |
|----------------|-------|-------|----------|-----------|
| Carbon..... | 52.48 | 52.49 | 52.49 | 53.22 |
| Hydrogen | 6.71 | 6.86 | 6.79 | 6.86 |
| Nitrogen | 16.32 | 16.18 | 16.25 | 16.48 |
| Sulphur..... | 0.45 | 0.48 | 0.47 | 0.48 |
| Oxygen | | | | 22.96 |
| Ash | 1.53 | 1.27 | 1.40 | |
| | | | | 100.00 |

It is evident from this analysis that the principal proteid extracted by water, is the same as that extracted by saline solutions, and as this substance is precipitated from the aqueous extract by dilution, it is undoubtedly dissolved by aid of the salts contained in the beans. It is not probable that the acid contained in the seed causes this solution, for in that case the proteid would not be precipitated by dilution, a considerable excess of acid being necessary to effect its precipitation. The meal after extracting with water, as just described, was treated with one per cent. sodium chloride solution, the extract filtered, largely diluted with water, and charged with carbon dioxide. Only a trifling precipitate resulted which, when prepared in the usual manner, weighed 0.52 gram. This preparation, 17, ash-free, contained 16.29 per cent. of nitrogen. These results show that nearly, if not quite as much of the globulin is extracted by water with help of the salts of the seed, as by use of stronger salt solutions.

[TO BE CONTINUED.]

A NEW AUTOMATIC PIPETTE.¹

BY EMIL GREINER.



WHEN taking a great number of samples in succession of the same volume of the same liquids, it is quite desirable to have a measuring instrument which will automatically take up the exact volume of liquid, without having to draw the same by mouth and watch for the mark, as is done when using the ordinary volumetric pipette. Therefore, I have devised an automatic pipette for such purposes, which is at present successfully employed in connection with the Babcock milk test. A glance at the accompanying cut will explain the practical value of this instrument, and as the pipettes can be made in all sizes required up to 50 cc., it can be adopted in many instances, where pipettes are used often and where accuracy is desired.

¹ Read before the New York Section, March 9, 1894.

NEW BOOKS.

AN ELEMENTARY MANUAL OF CHEMISTRY. BY FRANK H. STORER, AND WILLIAM B. LINDSAY, BEING A REVISION AND REWRITING OF PROFESSOR W. R. NICHOLS' ABRIDGMENT OF ELIOT AND STORER'S MANUAL. pp. 453. New York, Cincinnati, and Chicago: American Book Company. 1894. Price, \$1.20

This work, which as the authors aptly put it, "is the lineal descendant of the Eliot and Storer Manual and the Nichols' Elementary Manual," will be greeted by its former acquaintances with the consideration due the scion of an ancient family. To those who knew not its antecedents, may be said, "it is not written in the interest of any particular theory or of any one system of nomenclature or of notation." Starting with the physical and chemical changes familiar to every one, the air and the water—mixture and chemical compound—the elementary substances composing them are studied and with these the elements naturally grouped with them. Following these are chapters upon theory, the non-metals, the metallic elements, and the periodic law, closing with an admirable appendix upon chemical manipulation, a subject too often neglected.

Nearly one hundred pages have been added to the abridgment, largely to the theoretical and physico-chemical parts, which in the former edition were conceded to be scantily treated, although there is scarcely a chapter of the descriptive part to which important additions have not been made. The sections upon chemical calculations, atomic and molecular weights, Avogadro's law, empirical and rational formulas are clearly and concisely written and should present little difficulty to the student.

The book is peculiar in the attention paid to organic chemistry, which one hardly expects to find in a manual of this kind, nearly one fourth of the volume being devoted to this branch. The topics of flame and combustion, isomerism and the three important "series" of organic compounds are carefully explained and illustrated, closing with a chapter upon "some carbon compounds derived from plants and animals" embracing the sugars and allied bodies, the principal alkaloids and dyes and a few

pages upon physiological chemistry. Nor have the newer methods of industrial chemistry been overlooked, as for example, the Solvay process and the bi-sulphite process of paper manufacture; a brief outline of the metallurgical treatment of all the metals which are technically important, is also a valuable addition.

Some may note the brevity of the account of the action of nitric acid upon the metals, and regret the omission of the Raoult method of the determination of the molecular weight by the lowering of the freezing point, and notice some points in which the old usage has been adhered to, as for example the Chevreul explanation of the action of soap, and the symbol of arsenious oxide given as As_2O_3 .

The work, however, leaves little to be desired as a text-book of general chemistry in our higher institutions of learning and cannot fail to be of more than ordinary interest to the general reader.

A. H. G.

NOTES.

THE CHEMICAL MIDWINTER FAIR CONGRESS AT SAN FRANCISCO.

The great success of the international congress held in connection with the World's Fair at Chicago, in August, 1893, was probably the stimulating cause which led the chemists of the Pacific coast to organize a similar congress in connection with the San Francisco Midwinter Fair. The committee in charge of the congress consisted of Prof. W. B. Rising, chairman, Professors E. W. Hilgard, John M. Stillman, G. M. Richardson, A. L. Lengfeld and Messrs. W. M. Searby, Alfred Ropp, Edmond O'Neill, Harry East Miller, Theodore J. Wrampelmier and E. C. Burr. The sessions of the congress were held in Golden Gate Hall, 625 Sutter street, June 7, 8 and 9, 1894.

The attendance at the meeting was most gratifying in the number of chemists, although the public, not much interested in such matters, was but sparsely represented. Unfortunately, no record was kept of those in attendance and only an estimate can be made of the total number, but this was in excess of

fifty, showing the lively interest taken by the Pacific coast chemists in the success of the meeting. Only two cismontane chemists were in attendance.

In the arrangement of the program of the congress but little attempt was made to group the topics together by subjects, but the arrangement was simply such as was thought would best fill in the time. The titles of the papers read on each day of the session follow:

THURSDAY, JUNE 7, 10 A. M.

- Chairman W. B. Rising
1. Introductory Remarks James D. Phelan
 2. "Industrial Applications of Chemistry" W. B. Rising
 3. "A Theory of the Dissociation of the Products of Explosives" W. R. Quinan
 4. "Concerning the Conversion of Mechanical Energy into Chemical Action" J. M. Stillman
 5. "Achievements and Aims of Physical Chemistry" J. R. Trevor
 6. "Contraction of Aqueous Solutions of Acetone" Karl P. McElroy
 7. "Modern Conceptions of Affinity and Valence" S. W. Young
 8. "Analytical Notes" W. B. Rising
 9. "Determination of Nickel in Nickel-Steel" L. R. Lenox
 10. "Limitations of the Cyanide Process" C. W. Merrill
 11. "Device for the Adjustment of a Balance" Frank Green
 12. "Methods for Standardizing Reagents used in Acidimetry and Alkalimetry" C. G. Hopkins and G. C. Caldwell
 13. "A Volumetric Method for the Determination of Sulphuric Acid" H. H. Deubam and G. C. Caldwell

FRIDAY, JUNE 8, 10 A. M.

- Chairman H. W. Wiley
1. "Properties of Typical Florida Soils" H. W. Wiley
 2. "Hawaiian Soils and Notes on the Chemistry of Certain Hawaiian Esculents" A. B. Lyons
 3. "The Nitrogen Contents of Soil Humus" E. W. Hilgard and M. E. Jaffa
 4. "Oil Tests" F. Shapely
 5. "Chemical and Physical Properties of some California Vegetable Oils" W. C. Blasdale
 6. "Some Characteristics of California Wines" W. H. Krug
 7. "California and Nevada Shales and their Products" A. A. Cunningham
 8. "Hydrocarbons of the Pyridin and Chinoline Series in California Petroleums and Asphalts" Dr. Frederick Salathe
 9. "Saccharimetry in Medicine" A. E. Regensberger, M. D.
 10. "Kryolith and its Industrial Application" Theodore Armstrong

SATURDAY, JUNE 9, 10 A. M.

- Chairman Geo. C. Caldwell
1. "The Analytical Properties of Iron Phosphide and Phosphate" L. M. Dennis and B. S. Cushman
 2. "The Preparation of Crystalline Chlorides by Means of Hydrochloric Acid Gas" L. M. Dennis
 3. "Parapropionic and Metapropionic Aldehyde" W. R. Orndorff and Miss L. L. Balcom

4. "Determination of Alcohol in Fortified Wines"....T. J. Wrampelmier
5. "The Influence of Alum, Aluminum Hydroxide, and Aluminum Phosphate on the Digestibility of Bread"..
.....W. D. Bigelow and C. C. Hamilton
6. "Chrome Ore Industry".....H. G. Shaw
7. "The Education of the Technical Chemist".....J. M. Stillman
8. "The Teaching of Chemistry".....General Discussion

The sessions were held in the morning beginning at ten o'clock and continuing until one. After luncheon each day excursions were made in San Francisco and vicinity, to points which were of interest to chemists.

On Thursday afternoon the Pioneer White Lead and Color Works, the Golden City Chemical Works and the manufacturing establishment of Clinton E. Wonden and Co., were visited.

On the afternoon of Friday the Pacific Coast Borax Works at Alameda Point, and the chemical laboratory of the University of California at Berkeley, were the objective points. The greatest interest was manifested by the visiting chemists in the manufacture of borax. In Southern California there are immense deposits of crystallized hydrous calcium borate, the mineral known as Colmanite. This mineral is easily crushed and reduced to a fine powder in which condition it is mixed with natural sodium carbonate obtained from the alkali deserts and heated under pressure with water to cause the reaction to take place, by means of which the lime appears as a carbonate and the sodium as a biborate. The process although a simple one is quite complicated from a technical point of view, and the visitors were much interested and thoroughly entertained by the exhibition.

The new chemical laboratory of the University of California was also the object of the greatest interest and profit. This laboratory is built upon the most modern plan and combines most thoroughly, convenience for work and efficiency of ventilation. Every department of chemistry taught in the institution has a separate place in the laboratory and the desks, apparatus, store-rooms and laboratories were all inspected with much pleasure.

On the afternoon of Saturday an excursion was made to the Western Sugar Refinery, formerly known as the Spreckels Sugar Refinery, which is one of the largest and most complete works of the kind in the world. The whole process of refining sugar was thoroughly explained and the building and apparatus inspected from top to bottom.

From the sugar refinery the party passed to the inspection of the Union Iron Works and the Pacific Rolling Mills. The gigantic operations of these two factories in the building of the great war ships which have been constructed and are under construction at this place, were thoroughly explained. No part of the excursion was of more interest to the chemist than this. The Union Iron Works kindly placed at the disposal of the chemists their private tug for the purpose of carrying the party from San Francisco to Potrero and return. The sail on the bay was thoroughly enjoyed by all.

On Saturday evening a delightful banquet of an informal nature was held at which forty, all I hope immortal, sat down. The festivities of the banquet were continued until a late hour.

On Monday the chemists were invited to visit the California Powder Works and the Giant Powder Co., situated near the Southern Pacific Railroad, about thirty miles from San Francisco. Not a very large number was able to accept this invitation, but those who did go were fully repaid for the trip.

There is no space here for comments on the scientific papers read, but, an inspection of the titles will show the broad scope of scientific research covered by the papers presented to the congress.

The visiting chemists received every courtesy from their San Francisco brethren, and those having the congress in charge certainly deserve the heartiest congratulations for the successful way in which they carried it to a happy conclusion.

H. W. WILEY.

ERRATUM.—Page 514, fifth line from bottom of page, for "*proof* silver, etc.," read "*pure* silver, etc."

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CONTRIBUTIONS TO THE CHEMISTRY OF CERIUM.¹

BY L. M. DENNIS AND W. H. MAGEE.

THE mineral cerite was first found in one of the iron mines of Bastnäs, in Westmanland, Sweden. Its peculiarity was noticed as early as 1751 by Cronstedt,² and in 1784 it was analyzed by d'Elhuyar,³ in Bergmann's laboratory, and was considered by these two chemists to be a silicate of lime and iron. In 1803 the mineral was again examined by Berzelius and Hisinger, and by Klaproth, and nearly at the same time, but independently, they discovered in the mineral a new oxide. Berzelius and Hisinger named the earth *ceria*,⁴ after the planet Ceres which had been discovered two years before by Piazzi. Klaproth called it *ochroiterde*,⁵ from its brownish-yellow color. Fortunately the former name was adopted, for the latter name would have been a misnomer, since pure cerium dioxide, as we now know it, has a pale-yellow color.

From that time to the present, cerium and its compounds have frequently been the subject of investigation, but the work of the earlier chemists is not of direct importance, since the ceria upon which they worked was, as we now know, a mixture of various oxides, chief among them being those of cerium, lanthanum, and didymium.

In 1839, however, Mosander made known a discovery of the highest importance; namely, that ceria was not a simple oxide

¹ Read at the Brooklyn Meeting, August 15, 1894.

² *Sv. Vet. Akad. Handl.*, 1751, S. 227.

³ *Sv. Vet. Akad. Handl.*, 1784, S. 121.

⁴ *Afhandl. i. Fysik, Kemi och Mineral.*, 1, 58.

⁵ *A. Gehl.*, 2, 303; *Beiträge*, 4, 140.

but a mixture of at least two. The newly isolated earth he called *lanthana*, and this, in 1842, he split up into *lanthana* proper, and another oxide which he named *didymia*.¹

Dating from the time of Mosander's discoveries, the results of the various investigations upon cerium acquire, of course, much greater value, but the chemistry of this element and the other rare earths has remained one of the most difficult problems in the field of inorganic chemistry, chiefly because of the great similarity in the chemical behavior of these different elements and the consequent difficulty of separating any one of them completely from the others. Naturally, then, in an experimental investigation of the compounds of cerium, the first problem to be solved is the preparation of pure ceria.

I. SEPARATION OF CERIA FROM THE OTHER EARTHS.

The ceria was extracted from allanite from Amelia County, Virginia, a large amount of this mineral having been most kindly sent to us by Professor W. G. Brown, of the Washington and Lee University.

Nineteen hundred and twenty-four grams of the finely powdered allanite was heated in large porcelain evaporators with concentrated hydrochloric acid until the supernatant liquid became dark brown. The syrupy liquid was allowed to cool and was then poured off, the residual mineral being again treated in the same manner until it became grayish-white, three treatments of about ten hours each usually sufficing. A portion of the residue was then moistened with concentrated sulphuric acid and heated until all of the acid was driven off. The white residue was thrown, in small portions at a time, into ice-water, and to the filtered solution, oxalic acid was added. No precipitate resulted showing that the treatment with hydrochloric acid had removed all of the rare earths.

The rare earth chlorides, mixed with those of iron, aluminum, calcium, etc., were then diluted and filtered. A portion of this filtrate was treated with hydrogen sulphide for twenty-four hours, the solution being kept at 70°, but no precipitate appeared. The hydrogen sulphide was then expelled by boiling, the sulphur was filtered off, and the filtrate was added to

¹ *Förh. Skand. Naturf. Stockholm*, 1842, 387; *Phil. Mag.*, 28, 241; *Pogg. Ann.*, 56, 503; *J. prakt. Chem.*, 30, 276.

the original solution. This was oxidized by nitric acid and a concentrated solution of oxalic acid was then added in excess. The pinkish-white precipitate of the rare earth oxalates was allowed to settle, and the oxalates were then washed by decantation with hot water until the supernatant liquid was colorless. They were then digested in large evaporators with one per cent. hydrochloric acid until all iron had been removed and were then dried and ignited in a muffle furnace. The reddish-brown oxides resulting weighed 410 grams, a yield of over twenty-one per cent.

The oxides were dissolved in concentrated nitric acid. To facilitate solution sulphurous acid was added to one portion and oxalic acid to another, but with no perceptible benefit in either case. There were obtained four liters of an almost syrupy solution which showed the didymium absorption bands very strongly.

Many different methods for separating the ceria from the accompanying earths have been proposed but none of them seem to yield cerium which is completely free from lanthanum and didymium unless the method proposed be many times repeated. Mosander,¹ the earliest worker upon this problem, obtained a mixture of didymia and lanthana free from ceria by precipitating the mixed chlorides with potassium or sodium hydroxide and passing chlorine through the suspended hydroxides. Ceric hydroxide is oxidized to the insoluble ceric hydroxide while the hydroxides of lanthanum and didymium are changed to chlorides and dissolve. Jolin² found that the treatment must be made seven times before the ceria is completely free from didymia and lanthana. Popp³ added sodium acetate to the solution of the chlorides and ran in chlorine, the cerium being precipitated. Later instead of passing in chlorine gas he added sodium hypochlorite and boiled. Gibbs⁴ boiled the mixed earths with nitric acid (1:2) having first added considerable lead dioxide. Zschiesche⁵ heated the rare earth sulphates with red lead and nitric acid. In each of the last two methods ceric oxide is formed. Winkler⁶ separated ceria and didymia from lanthana by adding

¹ *Phil. Mag.*, 28, 241.

² *Bihang till K. Sv. Vet. Akad. Handl.*, 2, 14; *Bull. Soc. Chim.*, [2] 21, 533.

³ *Ann.*, 131, 359; *J. B.*, 1864, 195 and 702.

⁴ *Sill. Amer. Jour.*, [2] 37, 332.

⁵ *J. prakt. Chem.*, 107, 65.

⁶ *J. prakt. Chem.*, 95, 410.

mercurous oxide to the solution of the chlorides and then potassium permanganate until the solution is colored by the latter. Ceria and didymia are precipitated. Welsbach¹ precipitates the ceria by fractional crystallization as cerium ammonium nitrate. Bunsen first² proposed to ignite the oxides with magnesia, to dissolve out the ceria as cerium magnesium nitrate and then pour the solution of the latter into a large amount of very dilute nitric acid, whereby ceric oxide is precipitated. Later³ he abandoned this method and proposed instead the method which has been most employed for preparing pure ceria. A solution of impure cerium sulphate is poured into boiling water containing one part of nitric acid to the thousand, and basic cerium sulphate is thrown down. This procedure must be repeated several times and is also very wasteful because the yield is small, so that it can be used with advantage only on material that is already nearly pure. Brauner⁴ increased the yield by dissolving finally in nitric acid instead of in sulphuric acid, driving off the excess of acid and precipitating with boiling water containing nitric acid. Debray⁵ fused the nitrates of the earths with from eight to ten times their weight of potassium nitrate at a temperature between 300° and 350°. The nitrate of cerium is decomposed leaving the oxide which is insoluble in water. The other nitrates are undecomposed and are soluble in water. Many repetitions were necessary to free the ceria from the other earths. Pattinson and Clark⁶ heated the mixed chromates to 110° when cerium chromate decomposes to ceric oxide, the other chromates remaining unchanged.

For the separation of the ceria from the other earths in the allanite solution obtained as stated above, the authors first employed the Mosander-Jolin method which so eminent an investigator as Cleve has pronounced to be the best. The nitrate solution of the earths was diluted, potassium hydroxide was added in excess and well-washed chlorine gas was run into the solution for from four to five days. The white precipitate of

¹ *Monatsh. f. chem.*, 4, 630.

² *Ann.*, 105, 40.

³ *Pogg. Ann.*, 155, 375.

⁴ *Monatsh. f. chem.*, 6, 792.

⁵ *Compt. rend.*, 96, 828.

⁶ *Chem. News*, 16, 259.

the hydroxides soon changed to a dirty violet and became light yellow soon after the action of the chlorine began. The ceric oxide was washed by decantation until the wash-water gave no precipitate with ammonium hydroxide, this washing occupying nearly a week as the precipitate settles very slowly. The precipitate was then dissolved in hydrochloric acid and the treatment with chlorine was repeated. After seven complete treatments the concentrated solution of cerium chloride showed no absorption bands when a layer ten cm. thick was examined with a Krüss spectroscope. The solution was then nearly neutralized with ammonium hydroxide and hydrogen sulphide was run in for twenty-four hours, the solution being warmed to 70° . A very slight precipitate of copper sulphide resulted. This was filtered off, the hydrogen sulphide was expelled by boiling and the separated sulphur was removed by filtration. To the filtrate was added a concentrated solution of pure oxalic acid, a snow-white precipitate of the oxalates of the rare earths resulting. This precipitate was treated with a hot solution of hydrochloric acid (two per cent.) until the washing liquid failed to give a reaction for iron when tested with potassium sulphocyanate and ether. The oxalate was then dried and ignited in porcelain crucibles over the blast-lamp. The resulting oxide was of a pale yellow color resembling in tint very light chamois leather.

In the meantime the method of separation proposed by Debray was tried upon another portion of the rare earths. It was found that the melting point of the mixture of rare earth nitrates and potassium nitrate was usually about 325° . (The melting point of potassium nitrate is stated to be 339° .) Upon treating the fused mass with water it was found that the insoluble residue contained, even after two fusions, appreciable amounts of didymium. Since cerium nitrate begins to decompose at 200° and didymium nitrate at about 300° , the cause of the presence of didymium in the insoluble cerium oxide is evidently to be ascribed to the high melting point of the nitrate mixture employed by Debray. If then the melting point of the mixture could be lowered the probable result would be that less of the didymium nitrate would be decomposed and it seemed reasonable to expect that, by sufficiently depressing the melting point,

cerium oxide completely free from didymium might be obtained by a single fusion. With this end in view the potassium nitrate was replaced by sodium nitrate, the melting point of the latter, 316° , being somewhat lower than that of the potassium nitrate. But even with this salt more than two fusions were necessary to free the cerium from didymium.

Carnelley and Thomson¹ have shown that while potassium nitrate melts at 339° and sodium nitrate at 316° , a mixture of these two salts in molecular proportion melts at 231° . Consequently, this mixture was next tried with the rare earth nitrates, the details of the method being as follows:

The oxalates of the rare earths, after being freed from iron, as above described, are placed in porcelain evaporating dishes, the oxalates being covered by funnels of such size that when inverted they fit inside the edge of the evaporating dish. Concentrated nitric acid is now poured over the oxalates. Action begins at once in the cold, but it can be greatly hastened by warming on a water-bath. After the nitrogen oxides cease to come off, and the liquid has become clear, the solution, which should be so concentrated as to be syrupy in consistency, is poured while still hot into large porcelain crucibles half-filled with the well-ground mixture of potassium and sodium nitrates. About enough of the solution to completely cover the dry nitrates is poured in and the whole is thoroughly mixed by stirring.

For heating the crucibles a double air-bath was used. Both of the air-baths and the two covers were lined within and without with asbestos board. Through the two covers, openings were made through which thermometers could be introduced at various points within the inner bath. The crucibles were placed in circular openings cut in a piece of asbestos board, this board resting on pipe clay rods in the inner air-baths. The asbestos board was also pierced with many smaller openings to allow free circulation of air. The air-bath was heated by two Bunsen burners, the height of the flame being kept constant by means of "precision" gas-cocks.

After the crucibles have been placed in position the temperature is brought up slowly, too rapid heating being liable to cause

¹ *J. Chem. Soc.*, 53, 782.

the mass in the crucibles to swell and run over the edge. The two covers are placed in position, and a thermometer is inserted through the center opening to such a distance that its bulb is on a level with the bottoms of the crucibles. The heat is gradually increased until the thermometer shows a temperature of 300° in the inner bath. The mixture melts at a little below 230° , and decomposition of the cerium nitrate begins almost immediately. As the temperature rises the brown fumes come off copiously, the evolution gradually lessening as the heating continues. If, after removing the covers, it is seen that the evolution of gas from the fusion has entirely ceased, then the decomposition possible at the temperature employed is complete. This usually takes from four to five hours after the temperature has risen to 300° . It was found that the cerium nitrate is not entirely decomposed even when the temperature has been kept at 350° for some time, and also that if the temperature rises above 320° the cerium oxide will contain some didymium. After the evolution of nitrogen oxides ceases, the bath is allowed to cool rapidly since by so doing the solid mass can usually be removed by inverting the crucible and tapping the edge gently. If it cannot be removed in this way it can usually be loosened by throwing a jet of hot water around the upper edge. The removal of the mass in a solid block is of advantage since the condition of the decomposition may be judged by the color of the oxide which has collected at the bottom. If it is bright yellow or nearly white the ceria is probably pure, but if brownish in color then some of the didymium nitrate also has been decomposed.

The solid mass is now treated with hot water which dissolves all but the oxides. These are allowed to settle and the supernatant liquid is decanted off through a filter. More hot water containing from four to five per cent. of nitric acid is poured over the oxides and the liquid is brought to boiling and poured while hot through the filter. This is repeated six times and finally the oxides are washed with hot water alone, the washing being continued until the wash-water gives no precipitate with ammonia.

The oxides are dissolved by heating them with concentrated sulphuric acid until fumes of sulphur trioxide begin to escape,

allowing the mass to cool and then treating it with a large amount of water. More rapid solution can, however, be effected by throwing a jet of water upon the hot sulphates and stirring the mass constantly. There is some tendency to spatter, but solution is obtained in much less time and with much less water than in the first procedure. A concentrated solution of cerium sulphate thus obtained showed no didymium absorption bands in a layer thirty cm. thick.

To test the separation quantitatively, weighed amounts of pure cerium and didymium oxalates were mixed, the mixture was dissolved in nitric acid as above described and the mass was fused with the mixed alkali nitrates. The soluble portion from the first fusion was evaporated down and again fused with the alkaline nitrates, and this solution and fusion was repeated in all four times. The temperature during each fusion was about 300° . The insoluble cerium oxide resulting from the fusions was in each case free from didymium, and of the total cerium taken more than sixty-three per cent. was obtained completely free from didymium by the four fusions.

Another sample of the mixed nitrates was fused at about 350° . The layer of cerium oxide which collected at the bottom of the fused mass showed a brown coloration at the edges, and the insoluble residue after being carefully washed and dissolved in sulphuric acid gave the didymium bands clearly. The filtrate tested by the hydrogen peroxide method mentioned below showed some cerium still present with the didymium.

From the foregoing it will be seen that while the method is not quantitative it is nevertheless quite rapid and the yield is comparatively high. Its chief merit lies in the fact that the cerium oxide resulting from each single fusion is free from didymium, an advantage which does not seem to be possessed by the other separation methods with which the authors are acquainted.

II. QUALITATIVE TESTS FOR CERIUM.

Early in the work the necessity arose for testing various solutions and residues for the presence of traces of cerium, and a comparison of the different methods which have been proposed was made to ascertain which test was most distinctive and delicate.

Until 1864, when Gibbs¹ proposed his lead dioxide test for ceria, no satisfactory method for the qualitative detection of this earth was known. In 1882, Hartley² proposed a more delicate and also a more easily applied test, using ammonium acetate and hydrogen peroxide. In 1885, Lecoq de Boisbaudran,³ and also Cleve,⁴ observed that hydrogen peroxide gave to solutions of cerium salts, to which an excess of ammonium hydroxide had been added, a precipitate of the same color as that yielded by Hartley's reagents; namely, an orange-red. Sonnenschein,⁵ in 1870, had proposed the use of ceria as a test for strychnia, and Plugge⁶, in 1891, has reversed this, using strychnia as a test for ceria. Finally, Gibbs⁷, in 1894, has proposed to substitute bismuth tetroxide for lead dioxide in his test.

Hartley appears to have been the only observer previous to Plugge to test the delicacy of the reactions proposed. He found that if a quantity of a cerium salt, equivalent to one mgm. of the element, were dissolved in 100 cc. of water, the addition of ammonium acetate and hydrogen peroxide gave a distinctly brown or orange-red precipitate which could be filtered off, dried, ignited, and weighed. "Hence, we can separate one part of cerium from 100,000 parts of liquid."

To test the delicacy of these various reactions one-half gram of ceric oxide was dissolved, as sulphate, in a liter of water. Each cubic centimeter of this solution would contain one-half mgm. of ceric oxide. When one cc. of this solution was diluted to 100 cc., and five cc. of the diluted solution was boiled with excess of lead dioxide and nitric acid (1:2), a faint yellow tint was to be observed, but four cc. failed to yield a distinguishable color; that is, 0.025 mgm. can be detected in about seven or eight cc. The bismuth tetroxide detected 0.017 mgm. under the same conditions.

In testing Hartley's reaction, one cc. containing one-half mgm. was diluted to 100 cc., each cubic centimeter then containing

¹ *Am. J. Sci.*, [2] 37, 352.

² *J. Chem. Soc.*, 41, 202.

³ *Compt. rend.*, 100, 605.

⁴ *Bull. Soc. chim.*, [2] 43, 57.

⁵ *Ber. d. chem. Ges.*, 3, 631.

⁶ *Arch. d. Pharm.*, 229, 558.

⁷ *Am. Chem. J.*, 15, 546.

0.005 mgm. of ceria. When two cc. of this solution was diluted so much that with the solution of ammonium acetate and hydrogen peroxide it formed about four cc., a yellow color was visible, especially on looking downward into the test-tube held above a white surface; 0.01 mgm. of ceric oxide, or rather the cerium salt equivalent to this, can, therefore, be detected. Ammonium hydroxide and hydrogen peroxide gave as distinct a color with one cc., that is, Boisbaudran's test is twice as delicate as Hartley's.

Next, Plugge's strychnia test was tried and proven to be as delicate as he claims. The strychnia solution is prepared by dissolving one part of strychnia in one thousand parts of sulphuric acid. The solution suspected of containing ceria, or a few cubic centimeters of it, is rendered alkaline by sodium hydroxide, evaporated to dryness, and a drop of the strychnia solution is added. One-tenth of a milligram of ceria gives a distinct blue or violet color changing to red. One-hundredth of a milligram gives a faint blue tinge which rapidly fades. If oxalic acid be present it must be decomposed or the test fails. Boisbaudran's test is then the most delicate of any yet proposed.

Finally, known amounts of lanthana and didymia (mixed) and ceria in solution were mixed and Boisbaudran's test applied. A distinct coloration of the hydroxides was produced when 0.01 mgm. of ceria was mixed with 0.1 gram of lanthana and didymia in about 100 cc. of solution.

To apply the test in the presence of a large excess of other rare earths, very dilute ammonium hydroxide solution should be employed and this added drop by drop until the first permanent hydroxide remains after shaking. The hydrogen peroxide is then to be added—only a couple of drops are needed—and the mixture well shaken. By this means the weakly basic ceria is precipitated almost alone and the orange-red color cannot be disguised.

III. CEROUS CHLORIDE.

The ceric oxide, prepared according to the directions given in the first section, was purified from any thorium present, by boiling the oxalate (prepared from the sulphate) with a concentrated solution of ammonium oxalate. Any thorium oxalate dissolved,

was poured off and a similar solution poured over the residual cerous oxalate. The whole was then bottled and allowed to stand for some months with occasional shaking. The mixture was then brought to boiling and the liquid again poured off, the residual oxalate being washed with a similar solution. This washed oxalate was then dissolved in nitric acid, care being taken to ensure full decomposition and it was then almost neutralized with ammonium hydroxide. Potassium hydronitride was then added¹ so long as it continued to throw down a precipitate. This was filtered off leaving a solution of cerium nitrate containing only potassium and ammonium salts with possibly traces of calcium. This solution was precipitated with ammonium hydroxide and washed by decantation until a liter of the wash-water left no residue on evaporation. The ceric hydroxide was then tested for calcium, potassium, etc., with the spectroscope and proved to be free from all foreign material. This pure hydroxide has been employed to prepare salts of cerium.

As this work has been in reality only preliminary to an extended study of cerium, many of the already known salts were prepared in order to become familiar with their characteristics, but of these there is no need to speak at length.

A salt, which may probably be rightly claimed to be a new compound, was prepared while endeavoring to obtain cerium tetrachloride. This latter should be capable of existence if cerium is properly placed in the periodic system. Every other element in group IV of that system forms such a chloride not even excepting lead.² Among other attempts made, one was as follows: A concentrated solution of cerous chloride, obtained by dissolving ceric chloride in hydrochloric acid and evaporating was placed in a wash-bottle surrounded by a freezing mixture (snow and salt) and dry chlorine gas run in. This was rapidly absorbed, and after a short time a white crystalline mass settled out. This was placed on a porous porcelain plate to remove the greater part of the liquid, and then the following experiments were tried with different portions.

An attempt was at first made to dry it to constant weight over

¹ Dennis and Kortright, *Am. Chem. J.*, 16, 79.

² *Monatsh. f. Chem.*, 14, 505.

dry caustic potash in vacuo. A large, but irregular, loss of weight occurred and the crystals evidently effloresced. On exposing it to the open air again it gained in weight till almost as heavy as at first.

An attempt to dry it over calcium chloride gave a similar result. A portion was then dried in air, dust being excluded.

| | Grams. |
|------------------------------|--------|
| Weight of sample taken | 2.9824 |
| " " " after 72 hours | 2.9801 |
| " " " " 118 " | 2.9790 |
| " " " " 142 " | 2.9786 |
| " " " " 166 " | 2.9786 |

The chloride therefore assumes a constant weight in air.

In analyzing this air-dried chloride the cerium was first precipitated from the aqueous solution of the salt by ammonium hydroxide. The precipitate was so gelatinous that it was difficult to wash it free from chlorides and the oxide obtained by ignition of the precipitate was not of a pure yellow color. The percentages of cerium obtained in two analyses were 38.01 and 38.19.

In two other samples the cerium was thrown down by ammonium hydroxide and hydrogen peroxide was added. The orange-colored hydroxide thus formed was not as gelatinous as that formed with ammonia alone, and was much more easily washed, but on ignition of the precipitate the resulting ceric oxide was of a pale pink color. This color may have been due to the presence of a small amount of a higher oxide, for the results—38.01 and 37.93 per cent. cerium—while not agreeing as well as could be wished, were too high (see analysis below). The chlorine was determined by precipitation as silver chloride and the water by the method suggested by Kraut.¹

| | Calculated for
$\text{CeCl}_2 \cdot 7\text{H}_2\text{O}$. | Found. |
|----------------------------|---|--------|
| Ce..... | 37.63 | 37.97 |
| Cl..... | 28.54 | 28.58 |
| H_2O | 33.83 | 33.88 |

The above analysis showed that the compound formed by passing chlorine into a cold saturated solution of cerous chloride was merely a finely crystalline form of cerous chloride and not a

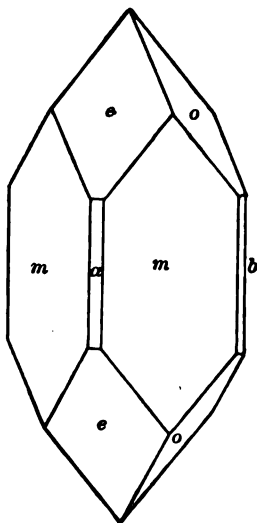
¹ *Ztschr. anal. Chem.*, 2, 242.

ceric chloride. Inasmuch then as the formation of the compound was probably due not to the oxidizing action of the chlorine, but to its dehydrating power, it seemed reasonable to expect that dry hydrochloric acid gas would accomplish the same result. The hydrochloric acid gas was made by the action of concentrated sulphuric acid upon solid ammonium chloride, the apparatus of Norblad being used for this purpose. Upon passing the gas into a cold concentrated solution of cerous chloride, the same white finely crystalline compound separated as with the chlorine. This was dried in the air to constant weight and then analyzed. In determining the cerium, the orange-colored hydroxide was precipitated by ammonium hydroxide and hydrogen peroxide but, before filtering, the solution was heated just to boiling. The suspended hydroxide changed to a bright yellow color but it did not become gelatinous and was easily washed. On ignition it yielded a ceric oxide of the usual pale yellow color.

| | Calculated for
$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. | | Found. |
|----------------------------|---|----------------|--------|
| Ce..... | 37.63 | 37.70 | 37.71 |
| Cl | 28.54 | 28.41 | 28.45 |
| H_2O | 33.83 | by diff. 33.89 | 33.84 |

The crystalline form of the chloride was kindly determined by Mr. A. S. Eakle, of the Geological Department of the University, who states that "the cerous chloride is orthorhombic in crystallization, and of the form shown in the figure.

The axial ratio $\overset{\vee}{a}:\overset{\vee}{b}:c = 0.80834:1:1.44187$.



$$a = \infty P \infty (100)$$

$$b = \infty P \infty (010)$$

$$e = P \infty (101)$$

$$m = \infty P \infty (110)$$

$$o = P \infty (011)$$

| Faces. | Angles measured. | Angles calculated. |
|-----------------|------------------|--------------------|
| $110:1\bar{1}0$ | $77^\circ 54'$ | |
| $110:\bar{1}10$ | $102^\circ 12'$ | $102^\circ 6'$ |
| $101:011$ | $49^\circ 20'$ |" |

The above chloride seems to be distinct from that obtained by Jolin¹ and by Lange² for which the formula $2\text{CeCl}_{15}\text{H}_2\text{O}$ is generally given.³ That chloride may be made by dissolving ceric hydroxide in hydrochloric acid and evaporating on the water-bath until the solution becomes quite viscous. This solution placed in a desiccator while hot solidifies on cooling to a crystalline mass of a yellow color. If these crystals be allowed to stand in the air, they lose their color and a glassy coating appears to form over the surface. The differences between the results obtained by Jolin and by Lange and the variation of each of their analyses from the calculated percentages made it seem desirable to repeat the analysis of chloride prepared by Jolin's method to see if better results could not be obtained. A sample of their chloride was therefore prepared by us and analyzed, but the results showed as great a variation from the theory as those already mentioned.

| | Calculated for
$2\text{CeCl}_{15}\text{H}_2\text{O}$. | Jolin. | Lange. | Magee. | Calculated for
$\text{CeCl}_{17}\text{H}_2\text{O}$. |
|----------------------|---|--------|--------|--------|--|
| Ce | 36.74 | 36.89 | 37.37 | 36.37 | 37.63 |
| Cl. | 27.87 | 28.40 | 28.80 | 28.65 | 28.54 |
| H ₂ O ... | 35.39 | | | | 33.83 |

IV. THE HYDROXIDES OF CERIUM.

The peculiar color changes of the hydroxides of cerium have often been noticed by chemists who have experimented with that element. When any one of the alkaline hydroxides is added to a solution of a cerous salt a white hydroxide is precipitated. This, so most authorities state, becomes slowly yellow on exposure to the air, more rapidly if chlorine or other oxidizing agents be present. Popp,⁴ however, claims that he obtained a dirty violet hydroxide by leading chlorine into a solution of a cerium salt precipitated by an acetate. This he claimed to be a higher hydroxide than the yellow. He states that it gave on ignition a red oxide. Others have claimed that his violet hydroxide was a basic acetate. Rammelsberg⁵ obtained a like-colored hydroxide by precipitating a hot solution of ceroso-ceric sulphate with caustic potash. Hermann⁶ and Stapff⁷ also obtained

¹ *Bull. Soc. Chim.*, [2] 21, 153.

² *J. prakt. Chem.*, 82, 129.

³ *Gmelin-Kraut, Dammer and others.*

⁴ *Ann.*, 131, 361.

⁵ *Pogg. Ann.*, 108, 45.

⁶ *J. prakt. Chem.*, 30, 189; 92, 113.

⁷ *J. prakt. Chem.*, 79, 257.

peculiar hydroxides to which they attempted without much success to assign formulas. Later Lecoq de Boisbaudran,¹ by the addition of ammonium hydroxide and hydrogen peroxide to a solution of a cerous salt, obtained an orange-red precipitate, which was studied by Cleve,² who, as a result of his observations, considered it the hydroxide corresponding to an unknown CeO_2 ; namely $\text{Ce}(\text{OH})_2$.

The following observations may throw some light upon the matter. A solution of mixed chlorides, containing lanthanum, didymium, and cerium was boiled and precipitated, while hot, with ammonium hydroxide. This was done in a large bottle which could be tightly corked. The mixed hydroxides were almost perfectly white, having possibly a faint pinkish tint. After the hydroxides had settled, the supernatant liquid was poured off and the bottle was refilled with thoroughly boiled distilled water. This was repeated until all foreign salts had been removed, the bottle being kept closely stoppered except while decanting and refilling. The hydroxides suffered no change of color upon standing for some days. Therefore, cerous hydroxide and the hydroxides of didymium and lanthanum when mixed are almost white. Didymium hydroxide by itself, however, or without much intermixture of white hydroxides, has a pinkish color. Finally air was blown through the suspended hydroxides. The color rapidly changed, at first to a dull purple and finally to a pale yellow.

Next a solution of cerous chloride was treated in the same manner. The hydroxide remained perfectly white while air was excluded, but, being exposed to air, it took on a dull purple color changing later to a bright yellow. Through another similar sample, air freed from carbon dioxide was passed; the same change in color resulted. Through yet another, pure carbon dioxide was passed. It remained white and did not change to purple even when, after some time, air was substituted for the carbon dioxide, the stability doubtless being due to the complete transformation of the hydroxide to the carbonate. Through yet another sample, air from which both oxygen and carbon dioxide were removed, that is, nitrogen, was passed. It remained white. Next a bottle was about one-

¹ *Compt. rend.*, 100, 605.

² *Bull. Soc. Chim.*, [2] 43, 57.

sixth filled with cerous chloride and this was precipitated—white—with ammonium hydroxide, and the bottle was then filled with unboiled water and lightly stoppered. The precipitate changed in color quite rapidly to light purple which gradually became darker from above downward and finally the top began to change to yellow. After about four months the upper third had become yellow, that below it being still violet.

Both the white and the purple hydroxides when washed on filter paper, dried at a low temperature and then ignited, gave an olive-green oxide, which did not become yellow even when the highest heat of the blast-lamp was applied. On powdering it very finely it seemed more nearly yellow. The weights seemed to agree well, however, with that called for by ceric oxide. The yellow hydroxide when dried and ignited gave a pale yellow ceric oxide. When the yellowish-white oxide prepared by this method or by igniting the oxalate is again ignited over the blast-lamp, but in an atmosphere of hydrogen, it becomes olive-green without marked loss of weight. For example 0.1263 gram of yellow oxide ignited in hydrogen weighed 0.1261 gram; 0.1574 gram similarly treated gave 0.1570 gram. When again ignited in air or oxygen, the oxide became yellow and regained its original weight. Bunsen¹ obtained very similar results.

As mentioned in a previous section, the precipitate obtained by the united action of ammonium hydroxide and hydrogen peroxide, on being dried and ignited, gives a pink oxide which seems to weigh somewhat more than ceric oxide, CeO_2 , should.

Another point, perhaps worthy of notice, was that when some of the purple hydroxide was dissolved in sulphuric acid and allowed to stand for a few days there separated out a crystalline sulphate which, on analysis, gave results too high for cerous and too low for ceric sulphate.

It is to be concluded, then, so far as the present observations go, that cerous hydroxide is white; that on exposure to oxidizing agents including atmospheric air it becomes first purple and then yellow, or, in other words, the purple hydroxide is an intermediate product.

¹ *Ann.*, 105, 40.

CORNELL UNIVERSITY, July 7, 1894.

METHOD FOR THE DETERMINATION OF THE FREEZING-POINT OF FATTY ACIDS.¹

By F. WOLFBAUER.

TRANSLATED AND ABRIDGED BY S. S. EMERY.

BY reason of the lack of agreement between different chemists in the determination of the freezing-point of a fat, and also because of the commercial importance of this determination as indicating the quality of fats, it seemed desirable that a standard method for this determination should be adopted.

Accordingly, my proposed method, after being carefully examined by Dr. R. Benedikt, Dr. von Perger, Dr. Ferd. Ulzer, and myself, was agreed upon by us as the method by which all future determinations of the freezing-point should be made.

The method is as follows:

One hundred and twenty grams of the fat is melted in a beaker at a temperature but slightly above its melting-point, mixed with forty-five cc. of caustic potash solution (1,250 grams of caustic potash in one liter of water²), and stirred until the fat is completely emulsified. It is then covered and kept at 100° C. for two hours, being occasionally stirred. A small portion is then tested by warming with alcohol (fifty per cent.) to ascertain whether saponification is complete, indicated by obtaining a clear solution; otherwise it must be replaced in the bath and there allowed to remain until this is accomplished.

The soap is now decomposed by boiling with 105 cc. of dilute sulphuric acid (sp. gr. = 1.143 = 18° B.³), preferably done in a silver dish, and continued until the free fatty acid rises to the top as a perfectly clear oily layer.⁴ The silver dish is then covered with an evaporating dish filled with cold water, to check the evaporation. The aqueous solution is then completely drawn off, and the fatty acid washed by boiling one-quarter of an hour

¹ From the Mittheilungen des Technologischen Gewerbemuseums, Wien, 1894.

² This solution should have a sp. gr. of 1.509, and contain forty-eight per cent. of potassium hydroxide.

³ Or a mixture of twenty-two cc. concentrated sulphuric acid and 150 cc. water.

⁴ If the size of the dish will permit of so doing, it is recommended to add (before decomposing) 150 cc. of boiling water, and allowing to stand ten minutes at 100° C.,—whereby the soap takes up water, rendering the subsequent decomposition more rapid

with dilute sulphuric acid (five cc. of concentrated sulphuric acid and 100 cc. of water). After settling and removing the dilute acid, it is boiled with 100 cc. of pure water,—this last being repeated should the washings taste distinctly acid. It is then dried in an open dish at 100° C. for two hours.

Only fatty acids obtained as above can be considered sufficiently pure and dry to be used for the determination of the freezing-point.

In the determination proper the following apparatus is employed: A thin-walled test-tube, three and one-half cm. by fifteen cm., is fixed by means of a cork in a suitable bottle. A Centigrade thermometer, extending from 1° to 60°, and graduated in fifths of a degree, is fixed in the test-tube by a second cork, which must be sufficiently loose to permit of an easy stirring of the contents of the tube with the thermometer. As the thermometer should be as short as possible, its scale is shortened by an enlargement blown in the bore in the interval between 2° and 28°. The amount of mercury *above* the surface of the fatty acid is thus diminished and a very appreciable error (a lowering of the freezing-point) is consequently avoided.

To accomplish the determination the test-tube is filled to within one cm., or one and one-half cm., of the top with the melted fatty acid, the thermometer immersed in the liquid to about the 35° mark (when the instrument should clear the bottom of the tube by about four cm. or five cm.), and the liquid stirred until it becomes quite opaque, and partial solidification sets in. Care should be taken at this point that the thermometer be not more deeply immersed, and after stirring rapidly in a circle ten more times, the thermometer is allowed to stand. The mercury now begins to rise in consequence of the latent heat liberated from the solidifying fatty acid; the highest temperature noted may be taken as the freezing-point.

The reading of the thermometer should be corrected for its inherent errors, previously determined. Its zero point should also be redetermined from time to time.

Each freezing-point determination should be repeated, and the difference between the two should not exceed 0.1° C.; as a rule it will not exceed 0.05°.

The use of narrower test-tubes than above prescribed, as well as lack of attention to other details, generally leads to low results, as a so-called "over-cooling" always appears in the passage from the liquid to the solid state.

The experiments which justified the adoption of this method were carried out in the following lines:

- I. The influence of the method of saponifying.
- II. The influence of the length of time of saponifying.
- III. The influence of the degree of dryness of the fatty acid.
- IV. The influence of the size and shape of the vessel in which the freezing-point is determined.
- V. The influence of a different length of thermometer.

I. The Effect of the Method of Saponifying.—The following determinations show that either an aqueous or an alcoholic solution of caustic potash may be used for the saponification:

| | Freezing-point found by means of | |
|--------------------|----------------------------------|------------------------------|
| | aqueous
saponification. | alcoholic
saponification. |
| Fatty acid I | 43.00° | 43.08° |
| Fatty acid II..... | 43.49° | 43.52° |

It should be here remarked that, in the case of alcoholic saponification, a one and one-half hours' boiling of the soap solution diluted with one liter of water is necessary to completely remove the alcohol.

II. The Influence of the Length of Time of Saponifying.—The two following determinations were made on the same fat; in I the time of saponifying was limited to one and one-half hours, while in II it was prolonged to fully fifteen hours:

| | Freezing-point. |
|-----------------------|-----------------|
| Determination I..... | 43.49° |
| Determination II..... | 43.44° |

It is therefore evident that a variation in the length of time of saponifying does not influence the final result.

Regarding the minimum length of time necessary, it varies with different fats,—slightly rancid fats requiring less than fresh fats, some of the former undergoing even spontaneous saponification on being mixed with the caustic potash. As a rule, however, for fresh fats two hours is amply sufficient, provided the fat was not melted at too high a temperature, and that, after

adding the caustic potash, a perfect emulsion was obtained by a vigorous stirring.

III. The Influence of the Degree of Dryness of the Fatty Acid.—

Comparative tests have shown most conclusively that by increasing the amount of water in a fatty acid the freezing-point is lowered, and *vice versa*. Further, as the absorbent power of fatty acids for water is less in the cold than at a higher temperature, it follows that during the cooling of a fatty acid, saturated with the maximum amount of water, at a certain temperature a separation of water must take place, shown by the still liquid fatty acid becoming turbid. This turbidity naturally interferes with the detection of solidification, and consequently, determinations made on undried or partially dried fatty acids show much less agreement with each other than those made on the perfectly dried acid. In two determinations on the same fat, using the undried fatty acid, were obtained the

| | |
|--|--------|
| freezing-points | 43.14° |
| and | 42.86° |
| the freezing-points differing by | 0.28° |

If, after washing a fatty acid, a filtration be substituted for the drying, a partial removal of the water is thus effected. But as the freezing-point of a fatty acid so treated is 0.3°–0.4° lower than one similarly treated, but also dried, it appears that such a filtration is entirely superfluous.

As is shown in the following table, it makes no difference in the final result whether the fatty acid be dried only one and one-half hours or a much longer time. It is also immaterial whether the dried fatty acid be used immediately for the determination, or whether it be first allowed to solidify and to stand a long or short time, being subsequently remelted for the determination.

RESULTS OF A SERIES OF DETERMINATIONS OF THE FREEZING-POINT OF A FATTY ACID, BY AQUEOUS AND ALCOHOLIC SAPONIFICATION, AND USING THE DRIED FATTY ACID.

| Determination. | The saponification | Further treatment | Freezing- | Difference |
|----------------|--|--------------------|--------------|-------------------|
| No | effected with and continued. | of the fatty acid. | point found. | from the average. |
| 1. | Aqueous potash.... 15 hours.... | Dried 5 hours.... | 44.44° | —0.02° |
| 2. | " " 1½ " | " 4 " | 43.49° | +0.03° |
| 3. | { A mixture of the above two dried fatty acids, washed again with water, filtered, and then dried two hours. | | 43.35° | —0.11° |

| | | | | | |
|---------------|--|-------------------------|--|--------|------------------|
| 4. | { The fatty acid from the above test after
standing twelve hours in the solid state,
and then heated one hour. } | | | 43.51° | +0.05° |
| 5. | Alcoholic potash... | $\frac{1}{2}$ hour..... | Filtered and dried
one hour. | 43.52° | +0.06° |
| 6. | Aqueous | " ... 3 hours.... | Not filtered, dried
two hours. | 43.45° | -0.01° |
| 7. | " | " ... | { The fatty acid from the
above test after solidifying,
immediately rinsed } | 43.46° | $\pm 0.00^\circ$ |
| Average | | | | 43.46° | |

IV. *The Influence of the Size and Shape of the Vessel in which the Freezing Point is Determined.*—To ascertain what influence is exerted by the use of a narrower test-tube than prescribed, the freezing-point of two fatty acids was determined in a tube only two and one-half cm. in diameter, as well as in one of the usual diameter, three and one-half cm., with the following results:

| | Freezing-point obtained | | |
|-------------------|-------------------------|---------------------|-------------|
| | in the wide tube. | in the narrow tube. | Difference. |
| Fatty acid I..... | 43.52° | 43.34° | 0.18° |
| Fatty acid II.... | 42.88° | 42.65° | 0.23° |
| Average..... | | | 0.20° |

These results by no means fix the allowable minimum diameter of the tube, as, *a priori*, the possibility is not excluded of obtaining a still higher freezing-point by the use of a tube of still greater diameter.

Accordingly, the freezing-point of the same fatty acid was determined, first, in a test-tube of the usual diameter, three and one-half cm., and then in a similarly shaped vessel having a diameter of seven cm., making about four times as much fatty acid around the thermometer in the second case as in the first. The freezing-points obtained were as follows:

| | |
|---|--------|
| In tube three and one-half cm. in diameter..... | 43.45° |
| " " seven cm. in diameter | 43.46° |

which show that the diameter of the tube may be increased from three and one-half cm. without disturbing the ratio between the amount of heat radiating from the fatty acid through the walls of the tube and the amount of liberated latent heat.

Consequently a tube three and one-half cm. or more in diameter answers perfectly for the correct determination of the freez-

ing-point, but it is not permissible to use one appreciably narrower than this.

V. The Influence of the Length of the Thermometer.—In order to demonstrate and also to estimate the error (a too low result) caused by an incomplete immersion of the thermometer in the liquid, thus allowing a portion of the column of mercury to project above its surface, the shortened thermometer recommended above, and a long (normal) one were first tested by a complete immersion in a water-bath, when each registered exactly the same temperature (43°); after which they were simultaneously placed in the test-tube containing water at 43° . The shortened thermometer was immersed to the 35° mark, leaving but 8° of mercury above the surface of the water, while the long thermometer could be immersed to only its zero mark, leaving fully 43° of mercury exposed. The whole was then placed in an air-bath, kept at a temperature of 20° in order to avoid the error of radiation. The reading of the long thermometer was about 0.13° below that of the shorter one.

This error was now calculated for each thermometer, giving, theoretically, for the long

| | |
|--------------------------------------|----------------|
| thermometer..... | 0.15° |
| while for the shorter one, only..... | 0.03° |
| the difference of..... | 0.12° |

being the theoretical error introduced by using a long (normal) thermometer, and agreeing closely with the experimental determination of the error (0.13°),

Though, of course, this error is not completely eliminated by using a shortened thermometer, still it is so reduced as to be of no practical importance.

RECENT WORK ON THE SUGARS.

By B. B. ROSS.

(Continued from page 553.)

Received May 14, 1894.

DETERMINATION OF WATER IN SUGARS.

Herzfeld (*Ztschr. des Ver. f. Rübenzucker*, **43**, 130, *Bull. Assoc. Chim. Belg.*, **6**, 267) reports the results of a large number of experiments in the determination of the amount of water in

syrops and sugars, the drying being effected both in air and in vacuo.

The drying in contact with air was conducted at a temperature of about 105°C. , the samples under examination being contained in nickel dishes about eight cm. in diameter and two cm. deep.

For syrups, three grams of material were employed, along with thirty grams of well-purified quartz sand.

In the water determinations in vacuo, a temperature of about 107°C. was employed, while in the experiments with Soxhlet's drying apparatus, the operation was conducted at about 103° – 104°C.

A syrup prepared by dissolving a definite weight of sugar in a known weight of water was used in a large number of the tests made.

After three hours drying in vacuo, the results secured closely approximated the theoretical figures, and at the end of five hours' drying the correspondence was almost exact.

In drying in air, eight hours were required to obtain results agreeing with the theoretical water content, and the loss in weight still continued, even after fifty-six hours' drying.

In the estimation of water in syrups, to which alkaline salts had been added, it was likewise found that concordant results could be most quickly secured in vacuo.

With raw sugars, as well as with syrups, the results by drying in air were quite appreciably higher than those secured in vacuo, especially where the drying was at all protracted.

For maintaining a temperature of approximately 105°C. , the author employs toluene between the walls of the drying apparatus.

Josse (*Bull. Assoc. Chim. France*, **10**, 656) proposes to employ in the determination of water in syrups and masse cuite, a dried and weighed spiral of filter paper which is to be saturated with the sample under examination.

A strip of filter paper, one to two cm. wide and about three meters in length, is coiled into a spiral form, placed in a capsule about seven cm. wide and two cm. deep, dried and weighed.

Two grams of syrup or masse cuite is next brought into the dish, about six to eight cc. of water added, and after the mixture has been warmed slightly the paper spiral is inserted.

The liquid is readily absorbed by the filter paper, and the drying is conducted at 100° – 110° C., until a constant weight is secured, about two hours being ordinarily required to complete the operation.

It is claimed that the method is accurate as well as rapid.

DETERMINATION OF ASH IN SUGARS.

Courtonne (*Bull. Assoc. Chim. France*, **10**, 223) describes in detail the method proposed by him for the determination of ash in sugars by ignition of the sample in the presence of ferric oxide. The process is conducted as follows:

Place in a platinum capsule two grams of freshly calcined ferric oxide, which should also have been thoroughly washed to insure freedom from sulphuric acid. Into the same vessel weigh five grams of sugar, or about two grams of molasses. After addition of a little water to the mass, the mixture is evaporated rapidly upon a sand-bath or a metallic plate and heated over a Bunsen burner until frothing takes place. The capsule is now placed in a muffle heated scarcely to dull redness; the combustion is found to take place quite rapidly, and the incineration is sometimes completed in a quarter of an hour—always within half an hour.

Among the advantages presented by this process, it is claimed that, as in the Alberti and Hempel method, where quartz sand is employed, the mass is well divided by the admixture with the ferric oxide, and the points of contact of the material with the air are thus multiplied. The formation of carbonates is also prevented and the ferric oxide facilitates oxidation by acting as a carrier of oxygen from the air to the sample; further, the low temperature employed prevents the loss of volatile salts, such as chlorides, while the rapidity of execution of the incineration is an important advantage.

This method should also have the preference over the quartz sand process for the reason that the platinum vessels used are much less readily attacked where ferric oxide is employed.

Vivien (*Bull. Assoc. Chim.*, **10**, 225) reports the result of experiments with Courtonne's method, employing different temperatures and different periods of time for the ignitions.

The results were found to be always lower than those secured

by the sulphuric acid method and the direct ignition process, the figures for the same sample not being at all concordant.

A constant weight was not obtainable by this process and the composition of the ash varied considerably with the length of time of the incineration and the temperature employed.

At somewhat elevated temperatures it was found that chlorides were more or less attacked and, possibly, partly volatilized.

ALBERTI AND HEMPEL'S METHOD FOR ASH DETERMINATIONS.

Stift (*Oest. Ztschr. Zucker*, **22**, 22; *Chem. Ztg. Rep.*, **17**, 102), as the result of a large number of experiments with different sugar products, concludes that this method, by proper and careful execution, and with previous thorough testing of the quartz sand employed, is to be most highly commended, yielding, as it does, concordant results and, in contrast to other methods, furnishing more correct and uniform figures for the content of inorganic substances.

A point of great importance in the performance of the incineration is the necessity of the employment of quartz sand of absolute and known purity.

With sugars containing considerable proportions of nitrates (which are decomposed in this process), it is necessary to make a separate estimation of nitric acid.

THE DETERMINATION OF VOLATILE AND INSOLUBLE FATTY ACIDS IN BUTTER FAT.

BY W. H. BEAL.

Received July 27, 1894.

A FEW years ago when called upon to make examinations of the fat in a number of samples of cream the author attempted to use for that purpose the then recently proposed method of Waller as modified by Moore¹ which is briefly as follows: Two and five-tenths grams of fat are placed in a weighed Erlenmeyer flask and saponified with one gram of potassium hydroxide dissolved in fifty cc. of seventy per cent. alcohol. After heating until saponification is complete the alcohol is driven off in a boiling water-bath. The resulting soap is dissolved in fifty cc.

¹ See *J. Am. Chem. Soc.*, **11**, 144, 1889.

of water and decomposed by means of twenty cc. of dilute sulphuric acid (one part of strong acid to ten parts of water). The flask is connected with a condenser and fifty cc. are distilled off, the distillate passing through a small filter in the mouth of the receiving flask. The distillate is titrated with one-tenth normal sodium hydroxide solution, using phenolphthalein as an indicator. Fifty cc. of water are added to the contents of the flask and an equal quantity distilled off and titrated as before. This treatment is repeated until only one-tenth cc. or less of soda solution is required to neutralize the distillate. After cooling, the liquid remaining in the flask is poured off from the solidified insoluble acids through the same filter used for the distillates. The insoluble acids are repeatedly washed with hot water until all traces of sulphuric acids are removed. The condenser is then washed out with hot alcohol and the filter exhausted with the same solvent, the washings being collected in the flask containing the insoluble acids. The alcohol is driven off and the flask and contents dried at 100° C. and weighed.

With proper precautions satisfactory results were obtained with this method, but the work had not proceeded far before grounds for the following objections became evident: (1) Saponification is slow and removal of the last traces of alcohol in the dilute solution recommended is difficult; (2) there is danger from violent bumping, which it was found impossible to entirely prevent; (3) there is danger of charring the fat adhering to the sides of the flask when the contents of the latter are reduced to a small bulk, causing the final insoluble acid to have a brownish color instead of a pale yellow color which is normal; and (4) inconvenience and loss of time is occasioned by the necessity of frequently replenishing the contents of the flask.

An attempt to devise a process which would in a measure, at least, overcome these difficulties, which it may be observed are in large part shared by all the methods now in vogue, resulted finally in the adoption of the following method of procedure:

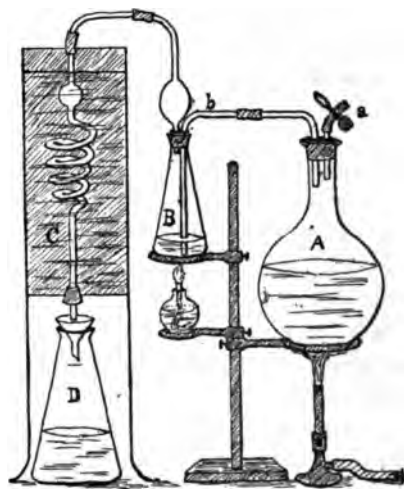
Volatile Acids.—Two and eight-tenths to two and nine-tenths cc. (approximately two and five-tenths grams) of the pure fat were measured by means of a narrow pipette into a weighed Erlenmeyer flask (long narrow form preferable) of 200 cc.

capacity. Saponification was accomplished by adding two cc. of a solution prepared by dissolving fifty grams of potassium hydroxide (free from carbonates) in 100 cc. of water and five cc. of strong (ninety-five per cent.) alcohol. The flask was connected with a reflux condenser and heated on a water or steam-bath until saponification was complete. Five minutes was usually amply sufficient for this purpose. The last traces of alcohol were quickly and completely removed with the filter pump by means of a device described by L. F. Nilson.¹

The soap thus obtained was dissolved in thirty cc. of warm water and decomposed with twenty cc. of a twenty per cent. solution of orthophosphoric acid. The volatile acids were expelled from the flask by means of a current of steam, using the apparatus described below. The operation was usually considered complete when 500 cc. had passed over, although, as an extra precaution, fifty cc. more was distilled over and titrated separately. For titration, decinormal soda solution and phenolphthalein were used.

The apparatus used in distilling is shown in the accompanying cut. A is a liter flask two-thirds full of water, which is kept boiling. The steam generated is forced into the decomposed

soap solution in B through the tube b, which reaches nearly to the bottom of the flask. This second flask is provided with a small lamp, so regulated as to prevent increase, by condensation, of the solution in the flask, and finally to bring its contents to a small bulk (about fifteen cc.). The condenser C consists of a copper tank, fifteen inches high, twenty inches long, and five inches wide, having four perforations in the bottom, into which glass spirals are fitted



by means of rubber stoppers, and provided with proper inlet and

¹ *Ztschr. anal. Chem.*, 28, 176.

overflow pipes for the water supply. Provision was thus made for four distillations at one time. The distillates were collected in wide-mouthed Erlenmeyer flasks, marked on the neck at 500 cc., and carrying funnels with small filters, through which the distillates passed.

Insoluble Acid.—After the distillation was completed, the condenser and connections were rinsed back with boiling water into the flask containing the non-volatile acids. The latter were shaken up with the hot water, and the solution, when cold, was passed through the same filter used for the distillate. Hot water (about 100 cc.) was again added, shaken up with the contents of the flask, and when cold filtered off as before. This operation was repeated until the washings contained no trace of phosphoric acid. The filter was then exhausted with hot, strong alcohol, and the solution allowed to run into the flask containing the insoluble acids. The alcohol was driven off on the water-bath and the fatty acids dried at 100° C. in the air-bath until they began to gain weight.

Very uniform and concordant results were obtained by this method in the examination of a large number of samples of butter fat.

The expulsion of the volatile acids by means of a current of steam, which it was afterwards found¹ had already been suggested by Goldman,² proved to be a decided improvement over direct boiling of the solution containing the fatty acids. When the operation had been started it required but little further attention and there was no danger of bumping or of overheating the insoluble acids. The volatile acids were very thoroughly removed, the last distillate of fifty cc. never requiring more than two-tenths cc. of soda solution for neutralization.

The first fifty cc. of distillate obtained by this method required less soda solution than that obtained by the Reichert or the Moore-Waller methods, and titration of each successive fifty cc. of the total 550 showed that expulsion of the volatile acids was much more gradual and uniform than in the latter methods.

¹ *Analyst*, Sept. 1892, 174.

² *Chem. Ztg.*, 1888, 12, 183; 14, 216; and 20, 317.

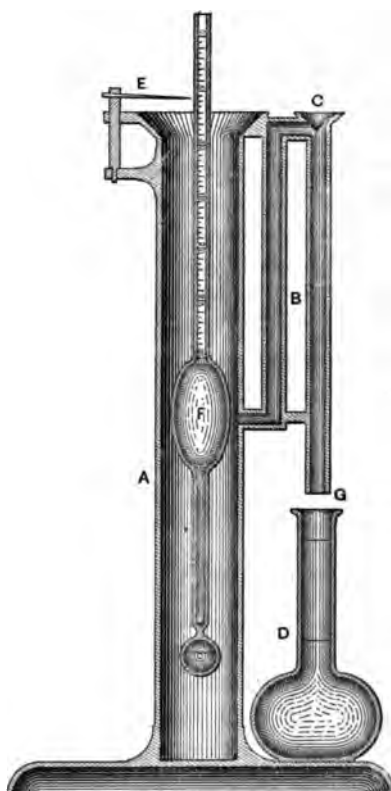
A GRAVIMETER FOR SUGAR ANALYSIS.¹

By W. K. GIRD.

Received June 28, 1894.

FOLLOWING is a description of the construction and operation of this apparatus; the drawing showing the instrument and appurtenances in section:

A represents the main tube to hold the solution under treat-



ment; B, overflow pipe; C, air vent to prevent siphonage, constructed in funnel form to facilitate cleaning; D, the usual graduated flask; E is an index finger pointing to the saccharometer, constructed so as to swing out of the way when necessary, and to stand for convenience of reading, say five graduations above the surface of the fluid; F, hydrometer or saccharometer, weighing exactly 26.048 grams; G, point of discharge into the flask D.

Although the operation is manifest, a few explanatory words may be appropriate.

The operator closes aperture G with his finger, then fills the main tube with the solution until it shows full at C, then strike off foam from the top of the main tube, remove the finger from G and permit the excess to escape to the last drop which must be removed.

This will leave the tube B moistened with the fluid under analysis, so that the condition will be left precisely the same as it will be after the delivery of the discharge hereafter explained,

¹ Read before the Midwinter Fair Congress of Chemists at San Francisco, June 8, 1894.

so that there can be no loss nor no gain either in quantity or quality. Next, place flask D under the overflow G and insert the saccharometer in the usual manner bring up the mouth of the flask so as to catch the last drop. The fluid in the flask will then be the required quantity. Now bring the point E to the index on the saccharometer and note the reading for Brix, to which add five, representing the height of the finger above the surface.

This instrument is constructed upon the sole principle of displacement determined by the weight of the saccharometer which displacement is always the same, not being affected by difference of temperature, rendering the use of the thermometer and corresponding tables unnecessary.

In taking the Brix as described above, the precise weight is conveyed into flask D through the overflow, thus dispensing entirely with use of the pipette and weighing as in the old system.

The results are absolute, doing away with all liability to error, inasmuch as no readings are necessary and all the manipulations are regulated and controlled by easily observed limitations.

In making many analyses as for instance in the laboratory at Chino numbering perhaps 200 per day, the advantages derived from the use of this instrument both in rapidity and accuracy can scarcely be estimated.

NOTE.—This instrument has since been improved, notably in the addition of a permanently attached thermometer which, in addition to the usual thermal graduations, has also a table on its face for the corrections due to differences of temperature.

ON THE QUALITY OF POTASSIUM IODIDE, SOLD IN THE MARKET AS U. S. P.¹

BY CHAS. O. CURTMAN.

Received August 4, 1894.

SIXTEEN samples were procured for examination by purchasing original packages made by twelve different firms. For six of them I am indebted to the courtesy of a friend, who bought them for a similar purpose and divided with me. To these, the tests of purity directed by the U. S. P. were applied seriatim, with the following results:

A. No residue should be left when one gram of the salt is dissolved in two cc. of diluted alcohol of sp. gr. 0.928. To this test fourteen specimens conformed; two left a small residue (Nos. 5 and 9).

¹ No. 5. Report Research Committee B.

B. To the test for excess of alkalinity the same fourteen specimens conformed, while two exceeded the limit (Nos. 5 and 9).

C. In the same two specimens and two others (5, 8, 9, 11), the flame test showed a considerable amount of sodium, while in the others the violet potassium flame appeared at once.

D. In both of these specimens (5 and 9) iodate was found (about 0.8 per cent.) while the others were free from it. (Nos. 5 and 9 were from the same firm.)

E. The hydrogen sulphide test showed the absence of metallic impurities in all of the sixteen specimens.

F. The barium chloride test indicated sulphate in five specimens (3, 5, 8, 13, 15); the others were free from it.

G. A small trace of nitrate was found, by reduction to ammonia, in three specimens (4, 7, 14); a somewhat larger amount in three others (3, 8, 13).

H. No iron could be detected in any of the specimens by potassium ferrocyanide.

I. Cyanide was absent in all specimens.

K. Titration with decinormal silver nitrate using potassium chromate as indicator, yielded with one gram each of the well-dried specimens as follows:

| cc. of $\frac{N}{10}$ AgNO ₃ required for one gram of specimen. | Per cent. of KI. | No. of specimens. |
|--|------------------|-------------------|
| 60.25 | 100.00 | 1, 10, 12 |
| 60.30 | 99.40 | 2 |
| 60.50 | 99.67 | 15 |
| 60.55 | 99.60 | 6 |
| 60.63 | 99.50 | 4, 7, 8, 11, 14 |

Making eleven specimens which conformed to the U. S. P. standard of at least 99.50 per cent.

| | | |
|-------|-------|------|
| 60.70 | 99.40 | 5, 9 |
| 60.75 | 99.33 | 3 |
| 60.80 | 99.30 | 16 |
| 60.85 | 99.20 | 13 |

Making five specimens below standard.

(The second decimal of a cubic centimeter was estimated on graduation into one-twentieth cc., where it fell between 0.00 and 0.05). Bromide could not be detected in any of the specimens.

Chloride was found in eight specimens (Nos. 3, 4, 5, 7, 13, 14, 15, 16), by precipitating with a slight excess of silver nitrate, washing thoroughly, and digesting for about twenty-five

minutes in a five per cent. solution of ammonium carbonate (free from hydroxide). The filtered liquid became turbid on acidulation with nitric acid.

Mohr's method of titration with decinormal silver nitrate, using potassium chromate as indicator, gives direct results when bromide and chloride are absent and the impurity consists of substances which do not precipitate silver nitrate. But when chloride is present (bromide is very rarely found in potassium iodide), its smaller molecular weight will require the use of a greater volume of silver solution than would suffice for pure iodide, and a calculation becomes necessary to obtain correct values. This may be avoided by reference to the following table, which, for potassium iodide containing chloride as only impurity, gives the percentage of pure potassium iodide corresponding to the number of cubic centimeters of decinormal silver nitrate used for one gram of specimen.

| cc. $\frac{N}{10}$
AgNO ₃ . | Per cent.
of KI. | cc. $\frac{N}{10}$
AgNO ₃ . | Per cent.
of KI. | cc. $\frac{N}{10}$
AgNO ₃ . | Per cent.
of KI. |
|---|---------------------|---|---------------------|---|---------------------|
| 60.2555 | 100.000 | 62.8 | 96.571 | 65.4 | 93.068 |
| 60.3 | 99.940 | 62.9 | 96.437 | 65.5 | 92.933 |
| 60.4 | 99.805 | 63.0 | 96.302 | 65.6 | 92.799 |
| 60.5 | 99.670 | 63.1 | 96.167 | 65.7 | 92.664 |
| 60.6 | 99.536 | 63.2 | 96.033 | 65.8 | 92.529 |
| 60.7 | 99.401 | 63.3 | 95.898 | 65.9 | 92.395 |
| 60.8 | 99.266 | 63.4 | 95.763 | 66.0 | 92.260 |
| 60.9 | 99.132 | 63.5 | 95.628 | 66.1 | 92.125 |
| 61.0 | 98.997 | 63.6 | 95.494 | 66.2 | 91.990 |
| 61.1 | 98.862 | 63.7 | 95.359 | 66.3 | 91.856 |
| 61.2 | 98.727 | 63.8 | 95.224 | 66.4 | 91.721 |
| 61.3 | 98.593 | 63.9 | 95.089 | 66.5 | 91.586 |
| 61.4 | 98.458 | 64.0 | 94.955 | 66.6 | 91.451 |
| 61.5 | 98.323 | 64.1 | 94.820 | 66.7 | 91.317 |
| 61.6 | 98.188 | 64.2 | 94.685 | 66.8 | 91.182 |
| 61.7 | 98.054 | 64.3 | 94.550 | 66.9 | 91.047 |
| 61.8 | 97.919 | 64.4 | 94.416 | 67.0 | 90.912 |
| 61.9 | 97.784 | 64.5 | 94.281 | 67.1 | 90.778 |
| 62.0 | 97.649 | 64.6 | 94.146 | 67.2 | 90.643 |
| 62.1 | 97.515 | 64.7 | 94.011 | 67.3 | 90.508 |
| 62.2 | 97.380 | 64.8 | 93.877 | 67.4 | 90.373 |
| 62.3 | 97.245 | 64.9 | 93.742 | 67.5 | 90.239 |
| 62.4 | 97.110 | 65.0 | 93.607 | 67.6 | 90.104 |
| 62.5 | 96.976 | 65.1 | 93.472 | 67.7 | 89.969 |
| 62.6 | 96.841 | 65.2 | 93.338 | 67.8 | 89.834 |
| 62.7 | 96.706 | 65.3 | 93.203 | 67.9 | 89.700 |

To avoid the error occasioned by potassium chloride, I repeated

some of the titrations with decinormal silver nitrate, using starch iodide as indicator (Pisani's method). A gravimetric method had been devised in 1872 at Goettingen, by Hübner, Spezia and Frerichs, in which thallous chloride was used as precipitant of iodides, and I concluded to convert this into a simple volumetric process and apply it to the present investigation. Thallous chloride, $\text{TlCl} = 239.07$, at 15°C. , requires 360 parts of water for solution (100 cc. of water dissolve 0.2777 gram of thallous chloride). A centinormal solution requires 2.3907 grams of TlCl for one liter. Thallous iodide, $\text{TlI} = 330.23$, at 15°C. requires nearly 12,000 parts of pure water for solution, and about 16,000 parts if potassium chloride be present or still more if the water be acidulated with acetic acid. Thallous bromide is much more soluble than the iodide, and its solution precipitates iodide promptly.

After a trial of various substances as indicators of the final point, spotting with sodium palladious chloride was found to yield very accurate results. The titration was conducted as follows: 0.16556 gram of potassium iodide (ten cc. of a solution, containing 1.6556 grams in 100 cc.) were placed into a capacious flask and centinormal thallous chloride added until spotting showed the disappearance of iodide from the solution.

For spotting, a ten per cent. solution of sodium palladious chloride was, by means of a pipette drawn into a broad line (two mm.) upon a plate of milk glass (photographers opal) and permitted to dry. As soon as it became doubtful whether further addition of thallous chloride produced a precipitate, a drop of liquid was taken out of the flask with a glass rod and drawn across the line of palladious chloride upon the plate. As long as iodide was present a dark spot formed at the crossing, and the number of cubic centimeters used was marked at its end in pencil. At the opposite end of the palladium line a drop of a saturated solution of thallous iodide was placed, so as to serve with its faint color for comparison with the drops taken from the flask. To guard against deception the same specimen was repeatedly tested by different operators, but the indications corresponded sharply.

The following results were obtained, with the first six numbers

of the specimens by the three methods: Mohr's with silver nitrate and potassium chromate (one gram of the specimen being used and the percentage corresponding to the cubic centimeters inserted from the table). Pisani's method with silver nitrate and starch iodide (1.6556 grams being used and each cubic centimeter of $\frac{N}{10}$ AgNO₃ deemed equivalent to one per cent. of KI) and with the thallous chloride, (0.16556 gram being used and one cc. counted as one per cent.).

| No. of specimen. | Mohr's method.
cc. used. | Per cent. KI. | Pisani's method.
Per cent. KI. | Thallous chloride.
Per cent. KI. |
|------------------|-----------------------------|---------------|-----------------------------------|-------------------------------------|
| 1..... | 60.25 | 100.00 | 100.00 | 100.00 |
| 2..... | 60.30 | 99.94 | 99.94 | 99.94 |
| 3..... | 60.75 | 99.33 | 99.20 | 99.20 |
| 4..... | 60.60 | 99.54 | 99.40 | 99.35 |
| 5..... | 60.70 | 99.40 | 99.30 | 99.30 |
| 6..... | 60.55 | 99.60 | 99.55 | 99.55 |

The method of Pisani and that with thallous chloride yielded somewhat less percentages with some of the specimens than Mohr's method, but gave, in almost every instance, results equal to each other.

SAINT LOUIS, MO., July 22, 1894.

SEWAGE DISPOSAL AT WORCESTER, MASS.

BY HARRISON P. EDDY.
Received February 6, 1894.

SINCE the description of the sewage disposal works at Worcester, by Dr. Leonard P. Kinnicutt, in 1891, (See *J. Anal. Appl. Chem.*, 5, 544), many important changes have been made both in the methods employed and machinery used. The capacity of the plant has also been greatly increased. The amount of water then dealt with was 3,000,000 gallons per twenty-four hours, while now between 10,000,000 and 15,000,000 gallons are successfully treated in the same time.¹

Before examining in detail the work accomplished it may be well to look briefly into the history connected with the purification of sewage at Worcester, that the problems encountered may be more fully understood.

For many years the city turned her sewage directly into the Blackstone river, a stream of about 23,000,000 gallons during

¹ Descriptions of this plant showing the engineering details are given in the *Engineering News* for January 11 and 18 and the *Engineering Record* for January 13, to which the reader is referred.

the summer months. This stream is fed, in part, by water from the northern water shed which tributary is called Millbrook, and it flows through the center of the city. This water amounts to about 8,000,000 gallons per day during the summer months. Millbrook being so conveniently situated was made the trunk sewer and to-day all the sewage of Worcester is discharged into it. For a number of years there was so little filth turned into the stream that the villages situated near the river, below the city, had little cause for complaint, but with the increase of population the river became very foul until, in 1886, the complaint from neighboring villages was heeded by the Massachusetts Legislature, and the right, granted in 1867, to turn sewage into the Blackstone river was revoked. An act was passed June 25, 1886, compelling Worcester to "remove from its sewage, before it is discharged into the Blackstone river, the offensive and polluting properties and substances therein, so that, after its discharge into said river * * * it shall not create a nuisance or endanger the public health." Four years were given the city in which to perfect some system for the accomplishment of this result, and accordingly, City Engineer Chas. A. Allen personally inspected works at home and abroad and after a careful study of the local problems recommended that a plant, capable of dealing with 4,500,000 gallons of sewage daily, be constructed and that the method of treatment employed be that of chemical precipitation.

This plant was first operated June 25, 1890, from which time until July, 1893, about 3,000,000 gallons of sewage were treated daily, except in time of storm when the entire flow was turned directly into the stream. It was found from the experiments of these three years that, by chemical precipitation, the sewage could be purified to an extent which would admit of its being turned into the river. Having settled this point, the next problem confronting the city was the treatment of the entire amount of sewage, as thus far only about twenty per cent. had been taken to the purification works. The actual amount of sewage is between 5,000,000 and 8,000,000 gallons per day, while the water from the brook, mentioned above, increases this to 10,000,000 or 15,000,000 gallons in dry weather, while in storm this amount is so largely increased that its treatment is wholly out

of question. The city is almost wholly sewered on the combined plan. From the start the plan had been to separate the waters of Millbrook from the sewage, thus leaving only a moderate amount of water with which to deal. On further consideration, however, it seemed advisable, for the present at least, to take as much of the sewage to the plant as possible. Accordingly, the present city engineer, then superintendent of the sewer department, Mr. F. A. McClure, proposed that ten additional settling basins, with the other necessary appliances, be provided, and that the whole, or as much as possible of the present flow be taken to the works. This plan having been adopted, work was begun in 1892 and the enlarged plant put in operation about the middle of July, 1893, since which time the entire flow has been treated.

The new basins differ somewhat from the old ones, being 166½ feet long and forty feet wide; the capacity is, however, the same, as are also the general features of construction. The effluent instead of returning to the steps provided in the old plant, is utilized to furnish power for pumping sludge during the day and for running a dynamo at night. A Shone ejector has been provided for pumping the sludge from the new work and part of that from the old. This ejector has proved to be very efficient and is much better adapted to use with sludge than the submerged centrifugal pumps employed on the original plant, as there is not the danger of clogging. It is run by air furnished by a compressor, power for which is derived from the water-wheel. Thus expense of steam is avoided.

The agitators originally used for mixing the chemicals have been taken out and two new tanks substituted; these are built of quarter-inch boiler steel and are set in masonry. These tanks are each sixteen feet long, eight feet wide, and three feet two inches deep. The bottom is fluted and through each of three valleys runs an iron pipe perforated with quarter-inch holes about fifteen inches apart. These pipes are connected by means of a main, four-inch pipe to an air receiver. Through the holes in these pipes air is blown at a pressure of sixty pounds, although so high pressure is not absolutely necessary and even air taken directly from the compressor has worked satisfactorily. This air agitates the liquid giving it the appearance of boiling.

The lime is thus thoroughly mixed with the water in the tank and runs from it in the form of milk of lime. The old practice of grinding the lime has been abandoned, it having been found that slaking in water was just as efficient and that a more economical use obtained by this thorough water-slaking before coming in contact with the sewage. By these changes a considerable saving in power used has resulted and, by the more thorough slaking of the lime, the amount required has been reduced about thirty per cent.

The treatment originally adopted as recommended by Engineer Allen, consisted in the addition to the sewage of lime and aluminum sulphate. It has been found, however, that the alumina need not be used, on account of the large quantities of iron sulphate contained in the sewage. This iron sulphate is not evenly distributed through the sewage of the day but comes at stated periods. At night, when the sewage is comparatively weak, that containing the copperas is stored crude in one or two of the settling basins and is used during the day, when there is a scarcity of iron and when otherwise aluminum sulphate should be added. By utilizing this iron sulphate, considerable expense is avoided and a perfectly clear, odorless effluent obtained. Lime alone is now added to the sewage, about 900 pounds being required for each million gallons. The highest grade obtainable is used, as it proves most economical in the end. The chemicals formerly entered the sewage just above the salmon ladder but have since been carried about 200 feet up the sewer, that a more thorough mixture might be obtained.

The chemical precipitation of sewage has been practiced in England for more than twenty-five years and yet, the published results of experiments performed there are so meager as to be practically of no assistance here. Consequently when this method was adopted in Worcester great faith had to be placed in future developments. From the first day the plant was operated, continued experiments have been made; at first these were wholly mechanical and random but it was soon found that a systematic study of the whole problem must be made if the work was to be successful. Accordingly the problems met in actual manipulation are made subjects of special investigation

in the well-equipped laboratories. That this move has been productive of good is shown by the reduction of nearly fifty per cent. in the cost of treatment, so far as effected by the chemicals used. Analyses of sewage and effluent are made daily. The samples for analysis are each composed of twenty-four portions taken hourly. Thus by averaging results for several days a mean is obtained, so that comparisons may be made with a certainty that the effluents correspond to the sewages. The percentage of impurity removed from the sewage is readily calculated and is indicative of the efficiency of the plant. Records of the analyses are kept in two forms: one is simply the numerical tabulation, the other a graphic illustration showing at a glance the result of treatment over any period of time. It will be noticed, from accompanying Table A, that the sewage dealt with is remarkably strong, considering that about half of it is water coming directly from North Pond. It is also interesting to note that the effluent contains only two and one-half parts per 100,000 parts matter in suspension and that of this only one and one-tenths parts are organic matter. Thus by treatment the organic suspended matter has been removed to the extent of 90.76 per cent. The total dissolved residue and the total and dissolved fixed residue are negative results, undoubtedly due to the large quantity of lime retained in solution in the effluent. From Table A the result of treatment of sewage since July can be followed by months, and the averages are given for the whole period. The work done as shown by the results of these analyses is very good and should fully carry out the object of the plant; *viz.*, not to transform sewage into a potable water, but to abate and finally terminate a nuisance to neighboring villages along the Blackstone river. During the last three years the sludge has been disposed of in various ways and numerous experiments have been performed and are now being carried on, which for lack of space cannot be described at this time. It may be added that the aim has been to make the plant attractive to the eye by the architecture of the new buildings, the lighting system and the grading around the basins, that the visitor may have his preconceived, erroneous impression of disagreeable sights and odors dispelled.

TABLE A.

| Date of Collection. | Residue on evaporation. | | | | | | | | | | Ammonia. | | | Oxygen Consumed. | | Chlorine. |
|--|-------------------------|-------------|-------------|-------------------|-------------|-------------|----------------|-------------|-------------|-------|-------------|-------------|-------------|------------------|-------------|-----------|
| | Total residue. | | | Volatile residue. | | | Fixed residue. | | | Free. | Albuminoid. | | Unfiltered. | Filtered. | | |
| | Total. | Dis-solved. | Sus-pended. | Total. | Dis-solved. | Sus-pended. | Total. | Dis-solved. | Sus-pended. | | Total. | Dis-solved. | | | Sus-pended. | |
| | | | | | | | | | | | | | | | | |
| Sewage, July 19-31, 1893..... | 70.2 | 48.0 | 22.2 | 32.1 | 17.9 | 14.2 | 38.1 | 30.1 | 8.0 | 1.043 | 0.622 | 0.403 | 0.219 | 5.62 | 3.18 | 6.64 |
| Effluent, "..... | 59.2 | 56.0 | 3.2 | 16.0 | 13.5 | 2.5 | 43.2 | 42.5 | 0.7 | 0.973 | 0.356 | 0.239 | 0.069 | 3.29 | 2.96 | 6.44 |
| Parts removed..... | 11.0 | 8.0 | 19.0 | 16.1 | 4.4 | 11.7 | 5.1 | 12.4 | 7.3 | 0.073 | 0.266 | 0.164 | 0.031 | 2.33 | 0.62 | 0.2 |
| Per cent. "..... | 15.67 | 16.67 | 83.39 | 50.16 | 24.59 | 82.39 | 13.39 | 41.20 | 91.23 | 42.78 | 40.69 | 46.58 | 41.47 | 19.5 | 19.5 | 2.99 |
| Sewage, Aug., 1893..... | 61.2 | 40.9 | 20.3 | 30.7 | 18.6 | 12.1 | 30.5 | 22.3 | 8.2 | 1.137 | 0.558 | 0.258 | 0.390 | 5.9 | 3.24 | 6.49 |
| Effluent, "..... | 53.9 | 50.7 | 3.2 | 14.9 | 13.5 | 1.4 | 39.0 | 37.2 | 1.8 | 1.083 | 0.333 | 0.254 | 0.069 | 3.7 | 3.42 | 6.49 |
| Parts removed..... | 7.3 | 9.8 | 17.1 | 15.8 | 5.1 | 10.7 | 8.5 | 14.9 | 6.4 | 0.054 | 0.225 | 0.066 | 0.231 | 2.2 | 0.18 | 0.00 |
| Per cent. "..... | 11.92 | 19.33 | 84.24 | 51.47 | 27.42 | 88.43 | 27.87 | 66.83 | 78.05 | 4.75 | 40.33 | 29.33 | 77.00 | 37.28 | 5.56 | 0.00 |
| Sewage, Sept., 1893..... | 62.1 | 43.4 | 18.7 | 29.3 | 17.0 | 12.3 | 32.8 | 26.4 | 6.4 | 1.488 | 0.522 | 0.247 | 0.275 | 5.11 | 3.15 | 6.16 |
| Effluent, "..... | 54.0 | 51.7 | 2.3 | 14.6 | 13.5 | 1.1 | 39.4 | 38.2 | 1.2 | 1.426 | 0.25 | 0.204 | 0.016 | 3.33 | 3.03 | 6.01 |
| Parts removed..... | 8.1 | 8.3 | 16.4 | 14.7 | 3.5 | 11.2 | 6.6 | 11.8 | 5.2 | 0.062 | 0.272 | 0.043 | 0.229 | 1.78 | 0.12 | 0.15 |
| Per cent. "..... | 13.04 | 19.13 | 87.70 | 50.17 | 20.59 | 91.05 | 20.12 | 44.70 | 81.25 | 4.17 | 52.11 | 17.42 | 83.28 | 34.63 | 3.81 | 2.43 |
| Sewage, Oct., 1893..... | 67.7 | 46.4 | 21.3 | 28.7 | 16.6 | 12.1 | 39.0 | 29.8 | 9.2 | 1.584 | 0.576 | 0.279 | 0.297 | 4.96 | 2.69 | 5.57 |
| Effluent, "..... | 54.0 | 51.6 | 2.4 | 13.3 | 12.5 | 0.8 | 40.7 | 39.1 | 1.6 | 1.504 | 0.288 | 0.214 | 0.074 | 3.37 | 3.13 | 5.31 |
| Parts removed..... | 13.7 | 5.2 | 18.9 | 15.4 | 4.1 | 11.3 | 1.7 | 9.3 | 7.6 | 0.08 | 0.288 | 0.065 | 0.223 | 1.59 | 0.44 | 0.74 |
| Per cent. "..... | 20.21 | 11.20 | 88.74 | 53.65 | 24.70 | 93.40 | 4.36 | 31.21 | 82.60 | 5.05 | 50.00 | 33.3 | 75.08 | 32.06 | 16.36 | 13.3 |
| Sewage, Nov., 1893..... | 57.5 | 41.7 | 15.8 | 22.8 | 13.1 | 9.7 | 34.6 | 28.6 | 6.0 | 1.548 | 0.45 | 0.22 | 0.23 | 4.49 | 2.14 | 5.69 |
| Effluent, "..... | 51.4 | 50.0 | 1.4 | 12.1 | 11.5 | 0.6 | 39.3 | 38.5 | 0.8 | 1.465 | 0.196 | 0.153 | 0.041 | 3.49 | 3.30 | 5.97 |
| Parts removed..... | 6.1 | 8.3 | 14.4 | 10.7 | 1.6 | 9.1 | 4.7 | 9.9 | 5.2 | 0.83 | 0.254 | 0.065 | 0.189 | 1.00 | 1.16 | 0.28 |
| Per cent. "..... | 10.69 | 19.91 | 91.11 | 46.93 | 12.21 | 93.80 | 13.58 | 34.61 | 86.67 | 5.36 | 56.44 | 29.54 | 82.19 | 22.27 | 54.2 | 4.92 |
| Av. of sewage analysis, July 19 to Dec. 1, 1893..... | 62.8 | 43.5 | 19.3 | 28.3 | 16.5 | 11.8 | 34.5 | 27.0 | 7.5 | 1.395 | 0.516 | 0.266 | 0.27 | 5.17 | 2.85 | 6.05 |
| Effluent "..... | 53.9 | 51.5 | 2.4 | 13.9 | 12.8 | 1.1 | 40.0 | 38.7 | 1.3 | 1.325 | 0.276 | 0.213 | 0.063 | 3.43 | 3.15 | 6.23 |
| Parts removed..... | 8.9 | 16.9 | 14.4 | 14.4 | 3.7 | 10.7 | 5.5 | 11.7 | 6.2 | 0.070 | 0.26 | 0.053 | 0.207 | 1.74 | 0.3 | 0.18 |
| Per cent. "..... | 14.18 | 18.40 | 87.56 | 50.88 | 22.43 | 90.67 | 15.94 | 33.33 | 82.6 | 5.010 | 48.49 | 19.88 | 76.67 | 33.65 | 10.53 | 2.98 |

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE
POLYTECHNIC INSTITUTE. IV.]

OIL-GAS.¹

BY W. A. NOYES, W. M. BLINKS AND A. V. H. MORY.²

SOME years ago Armstrong and Miller³ made a study of the gas made from petroleum by subjecting it to a high temperature, and of the oil deposited on condensing the gas. The following study of the gas made from petroleum by a somewhat different process and which gives in some respects different results may be of interest.

In the Pintsch system⁴ as described by Armstrong and Miller two D shaped retorts of cast iron are set one above the other, the largest size in use being six feet four inches long, ten inches wide and nine and three-fourths inches deep. The retorts are heated to a bright cherry-red and the oil may be run into the upper retort at the rate of about twelve and one-half gallons per hour. About eighty feet of gas per gallon of oil is considered a good yield.

By the Citizens Fuel and Gas Company of Terre Haute, gas is made from petroleum in large generators, one having a capacity of about 450 cubic feet of gas per minute, and two smaller ones with a capacity of 250 feet per minute, during the generation of the gas. The larger generator consists of an outer cylindrical shell of three-eighths-inch boiler steel, twenty feet high by eight feet in diameter, lined with fire-brick to a thickness of sixteen inches. The interior is composed of alternate chambers and checker-work compartments of fire-brick. Starting at the bottom there is an open chamber to the height of two and one-half feet, then, resting upon six twelve-inch arches, the checker-work of brick is built up, rows of brick, touching end to end and two and one-half inches apart, extending from wall to wall, composing the first tier, then upon these other rows are laid at

¹ Read at the Brooklyn meeting, August 15, 1894.

² The work described in this paper formed the basis of a thesis presented to the Faculty of the Rose Polytechnic Institute by Mr. W. M. Blinks and Mr. A. V. H. Mory for the degree of Bachelor of Science.

³ *J. Chem. Soc.*, (London) 49, 74, (1886).

⁴ *J. Soc. Chem. Ind.*, 1884, 463. We are indebted to Mr. W. B. Landon of Lafayette College for this statement, as the Journal is not accessible to us.

right angles to the first, then the next tier so as to be directly over the open squares formed by the first two rows, and so on, making the checkerwork to the height of five and one-half feet. The bricks are laid in, one upon another, without mortar or fire-clay.

Above this checkerwork is a chamber three feet high, then arches and more checkerwork for five and one-half feet and then another chamber extending to the top. A heavy iron door fourteen inches in diameter is provided at the top. By opening and shutting this it is made to act as a regulator for equalizing pressures when reversing operations. For heating the generator, oil is injected into the top and middle chambers by means of a steam-jet, air being admitted at the same points through five-inch valves. For generating gas, oil is injected into the top chamber through three jets. The gas which is formed leaves the chamber at the bottom through a sixteen-inch pipe lined with fire-brick and leading into the water-seal. The gas as it leaves the generator is too rich for burning in ordinary burners, hence in the seal-box it is diluted with ordinary air injected by steam through a four-inch pipe into the top of the seal. In the process as formerly used this air was injected into the generator with the oil and the oxygen which it contained appeared as carbon dioxide and carbon monoxide in the gas produced. This form of the process is still in use elsewhere.

The seal-box is three and one-half feet in height by four feet in diameter and the pipe leading from the generator dips eight inches below the water surface. A stream of cold water runs continuously into the seal-box, condensing the tar which is carried with the overflow water into the tar well. From the seal the gas passes through a tower scrubber twenty feet in height where it is washed with cold water, then through a tubular condenser, from this through a second scrubber and then through two purifying boxes, $14 \times 14 \times 3$ feet with a twenty-four inch seal. From the purifiers the gas passes through the station meter and thence to the holder. The purifying material used is technically known as Laming's Mass, and is prepared by treating wood shavings with copperas and lime, four barrels of copperas and about the same amount of lime being used to 300 bushels of shavings.

TEMPERATURE.

The destructive distillation of the oil in the process of gas-making is an endothermic operation, large quantities of heat being taken up from the hot brickwork, and the operation can only be carried on for from seven to ten minutes at a time, when the heating must be recommenced and continued for approximately the same length of time.

The temperatures in the generator were measured by noting the melting-points of salts. The salt was wrapped in platinum foil; this was placed in a sheet iron tube attached to an iron rod and the insertion was made through a hole in the side of the generator.

Measurements of the lowest temperature were made by introducing the salts immediately after the gas-making ceased and withdrawing them at the end of two minutes. Sodium chloride was unaltered in all trials at the first temperature, potassium chloride fused in about three minutes, while potassium bromide melted in less than two minutes. The lower temperature is, therefore, between the melting-points of potassium bromide and potassium chloride.

At the highest temperature sodium carbonate fused but calcium fluoride was unaltered. Experiments with sodium sulphate were rejected because the salt was apparently reduced by the gases to which it was subjected.

In assigning a temperature in degrees some difficulty is experienced, as authorities differ as regards the melting-points of these salts. The following values are given by Carnelly,¹ and quoted in the work of Mills and Rowan on fuels, page 341, and by Victor Meyer, and Riddle.² The values of the latter, however, are stated as being preliminary only and the melting-point of sodium carbonate especially, is stated, in a later paper, to be too high.

| | Carnelly. | Meyer and Riddle. |
|--------------------------|-----------|-------------------|
| Potassium bromide | | 715° C. |
| Potassium chloride | 734° C. | 766° C. |
| Sodium chloride..... | 772° C. | 851° C. |
| Sodium carbonate | 814° C. | 1098° C. |
| Calcium fluoride..... | 902° C. | |

The lower temperature may be stated with some degree of certainty as being about 750° C., while the higher temperature is probably 900° to 1,000° C.

¹ *J. Chem. Soc.*, [London] 1878 and 1880.

² *Ber. d. chem. Ges.*, 26, 2443.

COMPOSITION OF THE GAS.

The following determinations of the technical composition of the gas were made with Orsat's apparatus, the determinations of methane and hydrogen being made by explosion with an excess of air and the addition of oxyhydrogen gas, the large amount of methane rendering an explosion with air alone almost impossible. The illuminants were determined by absorption in fuming sulphuric acid. The first two determinations were duplicated with Hempel's apparatus with almost identical results. The "total carbon" in the gas was determined by exploding a known volume of the gas with an excess of air and determining the volume of carbon dioxide formed. The ethylene and propylene are calculated on the assumption that the illuminants consist exclusively of these two gases. It is well known, of course, and will be further shown below, that this is not the case, but for the purpose of calculating the heat of combustion of the gas the error introduced is slight and is certainly less than on the assumption, usually made, that the illuminants consist entirely of ethylene.

The heat of combustion is calculated on the basis of one cubic foot of the gas at 0° C., burned to carbon dioxide and vapor of water. The following values are used, deduced from the values given in Winkler's "Technische Gasanalyse."

| | | | | |
|--------------------------------------|----------------------------------|----------------------|----------------------|----------------------|
| One cubic foot of ethylene | gives 1573.3 English heat units. | | | |
| " " " propylene | " 2324.8 | " | " | " |
| " " " carbon monoxide | " 342.4 | " | " | " |
| " " " methane | " 964.3 | " | " | " |
| " " " hydrogen | " 289.8 | " | " | " |
| | Feb. 20.
Undiluted | Feb. 20.
Diluted | May 22.
Diluted | June 5.
Diluted |
| | gas.
Per
cent. | gas.
Per
cent. | gas.
Per
cent. | gas.
Per
cent. |
| Carbon dioxide..... | 2.3 | 2.1 | 0.7 | 0.8 |
| Illuminants | 28.1 | 19.9 | 19.3 | 15.9 |
| Oxygen | 0.2 | 5.9 | 7.0 | 7.7 |
| Carbon monoxide | 0.6 | 1.8 | 0.0 | 0.0 |
| Methane | 44.8 | 32.3 | 33.2 | 36.0 |
| Hydrogen | 20.5 | 14.2 | 6.9 | 6.1 |
| Nitrogen | 3.5 | 23.9 | 32.9 | 33.5 |
| | 100.0 | 100.0 | 100.0 | 100.0 |
| Total carbon—carbon dioxide..... | 115.7 | 85.6 | 85.5 | 77.0 |
| Illuminants { Ethylene | 16.2 | 10.3 | 6.3 | 7.5 |
| { Propylene | 11.9 | 9.6 | 13.0 | 8.4 |
| English heat units per cubic foot... | 1025.0 | 744.0 | 741.0 | 678.0 |

The small amount of carbon dioxide and carbon monoxide present in the gas is worthy of especial remark. Steam is used to inject the oil into the generator, but the analyses show that the steam must pass out at the end almost entirely unchanged. It follows from this that in an atmosphere of reducing gases and at a temperature of 700° to 900° C. it is impossible to burn carbon to carbon monoxide or dioxide by means of steam. This is still more apparent in those forms of the process in which air is introduced into the generator. One of us has made many analyses of gases produced in that way and in every case the oxygen of the carbon dioxide and carbon monoxide combined was less than that of the air introduced. These facts have a very important practical bearing as regards the use of steam with petroleum in the manufacture of gas.

The gas directly from the producer contained 1.83 grains of sulphur per cubic foot. The purified gas contained 0.025 grain per cubic foot.

EFFICIENCY.

The amount of oil required for 1,000 cubic feet of gas varies somewhat with the condition of the generators. The following determinations were made:

I. Feb. 20. One run of the large generator when it was about to be shut down for repairs.

| | |
|---|--------------|
| Oil per 1,000 cubic feet of diluted gas, for heating... | 2.3 gallons. |
| “ “ “ “ “ “ generating | 10.7 “ |

| | |
|------------|--------|
| Total..... | 13.0 “ |
|------------|--------|

II. June 5. Average of five runs of the large generator just fitted with new brickwork.

| | |
|---|--------------|
| Oil per 1,000 cubic feet of diluted gas, for heating... | 1.4 gallons. |
| “ “ “ “ “ “ generating | 9.7 “ |

| | |
|------------|--------|
| Total..... | 11.1 “ |
|------------|--------|

On comparing the analyses, it will be seen that the gas of June 5 was diluted somewhat more than that of Feb. 22, so that the real difference in efficiency is only about six per cent. As the oil used was different and that of June 5 was, apparently, of better quality, no reliance can be placed on the difference.

So much time was taken for other parts of the work that these

determinations were not repeated so many times as they should have been. Apparently, however, about ten gallons of oil are used in the large generator for generating 1,000 cubic feet of diluted gas and 1.5 to 2.0 gallons of oil are used for heating. When we consider the amount of the dilution, these results are somewhat lower than those reported by Armstrong and Miller. Unfortunately they give no analyses of the gas.

The oil used on Feb. 20 contained some water and an analysis gave

| | Per cent. |
|----------------|-----------|
| Carbon | 81.0 |
| Hydrogen | 12.7 |

The specific gravity was 0.843.

The oil used on June 5 was nearly free from water and had a specific gravity of 0.865.

We will take the run of June 5 as a basis for calculating, approximately, the efficiency of its plant. If we assume the oil to contain eighty-six per cent. carbon and fourteen per cent. hydrogen one gallon of the oil would give, when burned to vapor of water, about 140,000 English heat units, and the amount of oil required for the manufacture of one cubic foot of gas would give about 1,550 English heat units. Since the gas itself gives 678 units per cubic foot (see analysis), about forty-four per cent. of the heating power of the oil is found in the gas.

Without going into the details of calculation, it may be of interest to state that about thirty-five per cent. of the heating effect of the oil used in heating the generator, is lost by reason of the high temperature of the smoke gases, and an approximately equal amount of heat is carried away by the gas during the generation of the latter. It is probable that at least ten per cent. of the heating effect of the total oil used is lost in this way, though the calculations do not show quite that amount. The remainder of the loss appears to be due mainly to the formation of tar.

PHOTOMETRIC TESTS.¹

On May 21 a test of the candle-power of the diluted gas, as furnished to consumers, was made, using a Lumner-Brodhun

¹ These tests were made with instruments from the Physical Laboratory, and under the direction of Prof. C. L. Mees.

photometer with a three meter bar. The instrument was made by Hartman and Braun. The Methven slit was used as the direct standard, its value being first determined in terms of a standard amyl acetate lamp which was taken as of one candle-power. A wet meter, which, during one minute, indicated the number of cubic feet burned per hour, was used. Readings were taken on the meter and photometer each minute for five, and sometimes ten, consecutive minutes. Averages of these readings were made and the gas consumption was corrected for temperature.

The first night, tests were made using an argand, a five foot bat-wing, and a small and large Welsbach burner.

The second night, tests were made with a view to determining the relative efficiencies of different sizes of bat-wing burners, and of each size burning under different conditions. The conditions chosen were those of a smooth flame with a consumption rather under the indicated amount, and of a large, forked flame burning as high as possible without blowing. The appended table shows the results obtained,

MAY 22. METHVEN = 2.57 CANDLES.

| Burner | Candle power found during the test. | Rate of gas burned per hour during the test. | Candle power corrected for five feet per hour. |
|-----------------------|-------------------------------------|--|--|
| Argand..... | 29.3 | 5.17 cu. ft. | 28.4 |
| Five-foot bat wing... | 33.9 | 5.27 " | 32.2 |
| Small Welsbach..... | 31.4 | 3.25 " | 48.3 |
| Large Welsbach..... | 57.13 | 6.06 " | 47.1 |

MAY 23. METHVEN = 2.36 CANDLES.

| Nature of flame. | Burner. | As above. | As above. | As above. |
|------------------|-----------------|-----------|--------------|-----------|
| Smooth..... | 2 ft. bat wing. | 14.20 | 3.21 cu. ft. | 22.12 |
| Forked | " " | 23.32 | 5.54 " | 21.05 |
| Smooth..... | 3 " | 18.53 | 3.49 " | 26.54 |
| Forked | " " | 30.02 | 6.32 " | 23.75 |
| Smooth..... | 4 " | 19.66 | 3.43 " | 28.66 |
| Forked | " " | 37.45 | 6.74 " | 27.78 |
| Smooth..... | 5 " | 28.00 | 4.47 " | 31.32 |
| Forked | " " | 39.88 | 6.43 " | 31.01 |
| Smooth..... | 6 " | 25.01 | 3.96 " | 31.58 |
| Forked | " " | 45.01 | 7.06 " | 31.87 |
| Smooth..... | 7 " | 29.32 | 4.43 " | 33.10 |
| Forked | " " | 53.18 | 8.27 " | 32.15 |

It will be seen that the larger burners are most efficient and that, with one exception, the smooth flame gives better results. This is especially true of the smaller burners. A sample of the gas taken on May 22 gives for the calculated heating effect 741 English heat units. The statement of the analysis is given elsewhere.

COMPOSITION OF THE ILLUMINANTS.

In order to determine the presence and the amount of benzene and similar hydrocarbons in the gas, these were determined by a modification of the method of Hempel and Dennis, (see next paper), and also by absorption in absolute alcohol and subsequent dilution with salt water. Both methods gave essentially the same result and showed that about 1.2 per cent. by volume of the gas consists of the vapor of these hydrocarbons. From the oil obtained by the second method pure metadinitrobenzene was easily obtained by nitration and crystallization.

To determine the composition of the other gases forming the illuminants, gas directly from the generator was aspirated through an absorption train consisting of two one-liter bottles packed in ice to condense the tar, then two one-half liter bottles half filled with an ammoniacal solution of cuprous chloride to absorb acetylene, next a bottle of the same size half filled with dilute sulphuric acid to absorb ammonia fumes from the cuprous chloride solution, next three Drechsel wash-bottles standing in ice-water, the first two containing one hundred grams each of bromine with about half an inch of water above, and the third containing distilled water for the collection of bromine carried over from the other two, and finally a wash-bottle half full of a solution of sodium hydroxide to absorb bromine fumes. Approximately 125 liters of gas were passed through the train to effect the saturation of the bromine.

The bromine compounds were washed twice with caustic soda, then with distilled water, were separated, dried with calcium chloride, and fractioned. More than one-half came over between 127° and 150°. The residue remaining in the distilling bulb solidified on cooling. It was crystallized from alcohol and from ligroin when it melted at 113°-113.5°. An analysis gave the following results:

0.0750 gram gave 0.1500 gram AgBr.

| | Cal. for $C_4H_4Br_4$. | Found. |
|---------|-------------------------|--------|
| Br..... | 85.56 | 85.11 |

Armstrong and Miller¹ obtained a bromide melting at 116°, which they considered to be divinyl tetrabromide (1, 2, 3, 4 tetrabrombutane). The substance described above was probably the same, but less pure, as we have worked with much smaller quantities.

The portion of the bromides boiling from 127° to 150° was redistilled and gave three fractions, the largest 129°–133°, that from 133°–139° next and that from 139°–143° least. After fractioning again, a determination of the molecular weight by the air-displacement method of Victor Meyer, was made with the portion boiling at 130° to 133°. The results agreed fairly with the molecular weight of ethylene bromide. Determinations of the molecular weight of the fraction 140°–143° were unsuccessful owing to decomposition of the bromide. There can be little doubt, however, that the bromides consisted chiefly of ethylene and propylene bromides, the former being present in much larger amount than the latter.

A considerable precipitate was obtained in the ammoniacal solution of cuprous chloride, indicating the presence of appreciable amounts of acetylene and its homologues. In this respect our results differ from those of Armstrong and Miller.

TAR.

The amount and character of the tar varies considerably with the conditions of running. Two samples of the tar were examined, one which was thick and viscous, another which was comparatively thin. No essential difference in qualitative composition was established. The lower boiling substances contained in the tar were separated by distillation with superheated steam, the higher boiling products by direct distillation. In the direct distillation much trouble was experienced from frothing and it was found necessary to heat the tar at first in small quantities in an open dish until the frothing ceased. The residue was then distilled as usual.

Without going into the details of the work the results of the study may be stated briefly as follows:

¹ *J. Chem. Soc.*, (London) 49, 81, (1886).

Benzene and its lower boiling homologues appear to be present in the tar in only small amount. No positive evidence of their presence was obtained, although it has been shown that benzene is present in the gas.

Naphthalene is present in considerable amount and was identified by melting-point and boiling-point.

Anthracene is also present and was identified by melting-point and by conversion into anthraquinone. An approximate quantitative determination of the amount of anthracene was also made, showing the presence of about 0.35 per cent.

From the portion coming over at about 425° there was obtained, by crystallization, a solid melting at 250° and probably crysene.

From the portion boiling still higher a green crystalline solid melting at about 240° was obtained but not in sufficient amount for its identification.

Attempts to isolate phenol were unsuccessful, though it is probably present in small amount.

The results of the investigation confirm the conclusion of Armstrong and Miller that benzene and allied hydrocarbons may be formed, at high temperatures, from hydrocarbons which bear no simple relation to them.

In conclusion we wish to express to Mr. J. J. Kirkham, Superintendent of the Terre Haute Citizen's Fuel and Gas Company, our thanks for many favors shown us in the course of the work.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. V.]

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.¹

BY W. A. NOYES AND W. N. BLINKS.

SOME time since Hempel and Dennis² described a method of determining benzene vapors in illuminating gas which depends on their absorption in a very small quantity of absolute alcohol. The amount of mercury required and the difficulty of applying the method as described by these authors led us to

¹ Read at the Brooklyn meeting, August 15, 1894.

² *Ber. d. chem. Ges.*, 24, 1162. Also the translation of Hempel's Gas Analysis by L. M. Dennis, p. 221.

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attempt the determination with the use of a Bunte burette. The results were so satisfactory that it seems worth while to describe our method of procedure.

One hundred cc. of gas are taken in the burette and measured, either as usual, with a column of water of definite height above, or, perhaps better, with a side tube or bottle attached below so that the gas is brought to atmospheric pressure. The water is then completely removed from the cup of the burette above and the water in the burette is drawn down to the lower stop-cock as usual for the introduction of reagents. Instead of introducing the alcohol from below, however, two or three cc. of absolute alcohol are poured into the cup above and allowed to enter the burette, one cc. at a time. After each admission of the alcohol enough time is given for it to thoroughly run down before more is admitted and care is taken that the walls of the burette are uniformly moistened with the reagent. After withdrawing the alcohol below in the usual manner, two or three cc. of water are admitted above and withdrawn below and then more water is admitted above till the gas is brought to the original pressure, and the volume read.

To test the accuracy of the method, several determinations of the amount of benzene in the gas described in the last paper, were made. This gave 1.2, 1.3, 1.2, 0.5, and 1.2 per cent. The fourth determination was evidently in error for some unknown reason.

Twelve cubic feet of the same gas were passed through a meter, then through two large calcium chloride drying tubes, and then through three Drechsel wash-bottles containing absolute alcohol and a fourth empty bottle to condense vapor carried over, all being surrounded by ice. On dilution with salt-water, 16.8 cc. of liquid hydrocarbons were obtained. Considering these hydrocarbons to consist of benzene they would occupy in the form of vapor at 20° a volume of 4.46 liters. Twelve cubic feet are equal to 340 liters, of which 4.46 liters is 1.31 per cent. When we consider that a portion of the hydrocarbons obtained must have consisted of toluene, naphthalene and other hydrocarbons, whose vapors would occupy a smaller volume than benzene for a given weight, the agreement is satisfactory.

A DEVICE FOR THE ADJUSTMENT OF A BALANCE.¹

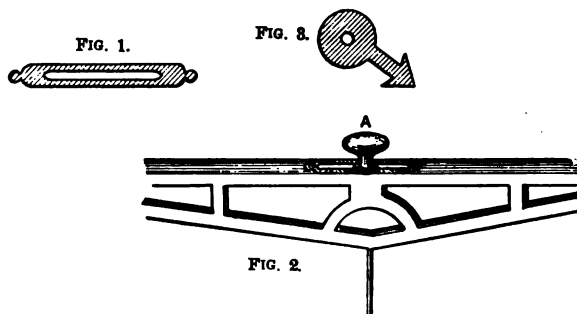
BY FRANK T. GREEN.

Received July 27, 1894.

IT is a matter of surprise to intending purchasers that some sensitive balances lack a method of adjustment. I do not allude to the analytical balance only. The assay, prescription, or pulp balance, often has this important improvement wanting. It is well known that the method of adjusting by screws on one or both ends of the beam is satisfactory. Also, that by means of a flag on the top and center of the beam—frequently used by Oertling—a wonderfully close adjustment can be reached.

It is not the intention to criticise these methods, but rather to show how an instrument lacking these improvements can be made adjustable by a person not a mechanic.

By means of a small strip of metal, fashioned after Fig. 1, and



preferably made of brass, any balance having a center screw on top of beam A can be made adjustable.

Fig. 1 represents such a device to be fastened to the top of beam in the center in such a manner as to slide either to the right or left as required. When the point of adjustment is reached it can be fixed by tightening the central screw, Fig. 2.

The strip, Fig. 1, or the arrow, Fig. 3, can be made in a few minutes of tinned iron, brass, or sheet proof-silver. The latter metal always being at hand in an assay office. The arrow method being adjusted by turning either to the right or left.

¹ Read at the Midwinter Fair Congress of Chemists, San Francisco, June 8, 1894.

NOTE ON A FORM OF SILVER OBTAINED IN THE REDUCTION OF THE SULPHIDE BY HYDROGEN.¹

BY FRANCIS C. PHILLIPS.

Received July 2, 1894.

IT is a well-known fact that many of the metals are reduced from their oxides, sulphides, and other compounds by hydrogen at high temperatures.

In the majority of such cases the form in which the metal is set free depends upon its fusibility. When both the metal and its compound are fusible only at temperatures far above that at which reduction by hydrogen occurs, the reduced metal usually retains the form originally possessed by its compound, becoming, however, somewhat more porous. Iron reduced by hydrogen from the oxide, sulphide, or chloride, appears as a porous mass or fine powder. The same is true of platinum and of copper.

In the case of other metals, the character of the original compound may exercise a determining influence on the form of the metal after its reduction.

If silver chloride be heated in hydrogen to about 300° C., reduction occurs with formation of hydrogen chloride. The reduced silver appears as a compact, rounded mass, somewhat rough, and having a moderate degree of luster. On heating precipitated silver sulphide in hydrogen, a decomposition occurs with formation of hydrogen sulphide at about the melting-point of silver chloride (450° C.).

The reaction is slow at this temperature, but is more rapid at a somewhat higher heat. The dull, black powder soon begins to assume a slightly lustrous appearance, and at the same time changes gradually into a mass of tangled wires or threads, which lose the black color of the sulphide and exhibit the luster of highly burnished silver. These vary in thickness from that of the finest hairs to that of coarse sewing-thread. They are so linked and knotted together as to be almost inextricable. Under

¹ First printed in Proceedings of Chemical Section, Eng. Soc., W. Pa., April, 1894; communicated by the author.

a microscope it can be readily seen that some of these wires are made up of many smaller ones, which are often imperfectly twisted together, giving the appearance of a rope whose strands had become partly untwisted. Closely-wound coils are often visible. Many of the wires seem to have the smaller ones of which they are composed welded into a single wire, the sides of which then have a fluted or grooved appearance. Owing to the open spaces left in such a mass, a considerable expansion occurs during the reduction. In several trials it was found that the volume of the mass of reduced silver was about three times that of the original sulphide. Experiments made with argentite, the native silver sulphide, using a piece about three cm. thick, led to similar results. The facets of the crystalline mass did not change their shape, nor was their luster much diminished, but a great number of fine wires of lustrous silver seemed to grow out from the mineral in all directions.

Silver sulphide heated in natural gas gave results like those obtained in hydrogen.

Stephanite, Ag_3SbS_4 , although fusible in hydrogen with evolution of a little hydrogen sulphide, yielded no silver at a temperature of dull redness.

Copper sulphide, artificially prepared, was slowly reduced by hydrogen at about the melting-point of barium nitrate (600°) with gradual formation of lustrous threads of copper very similar to those obtained in the case of silver.

The observation that silver and copper may be obtained in the form of wires by reduction of the sulphides is not new.

Opificius (*Chemiker Zeitung*, 1888, 649) announced that such a change occurs.

Bischof (*Annalen der Phys. und Chem.*, 1843, 289) describes experiments in which silver sulphide heated in steam to the temperature of boiling sulphur was reduced, yielding wire silver, the sulphur of the sulphide at the same time being oxidized to sulphuric acid. Bischof compares this change of crystalline argentite into wire-like forms of metal on reduction to the alteration of augite into asbestos.

Hampe (*Chemiker Zeitung*, 1893, 1692) has shown that copper in moss-like forms is produced on heating copper sulphide

with filings of the metal to a temperature above the melting-point of copper. The author supposes that copper is dissolved by the fused sulphide and set free again on cooling, being forced out from the fluid interior through the pores of the nearly solid crust in wires or threads. Similar experiments by this author in heating silver with silver sulphide yielded the metal in form of imperfect crystals instead of wires. It is not easy to account for the fact that silver can assume the form of wires or threads so readily on reduction of the sulphide. The fusing-point of silver is 500° higher than the temperature of reduction, and it does not seem possible that the peculiar form of the silver can have been caused by fusion of the metal. Nevertheless, its appearance suggests that it has passed through a liquid or plastic condition. It might seem possible that by the heat of reaction between the silver sulphide and hydrogen silver, at the moment of its reduction, the silver had been heated locally to fusion. The heat of formation of silver sulphide (three calories) is, however, nearly as great as that of hydrogen sulphide (7.2 calories). Hence the heat of reaction could not suffice to fuse the silver. Nor does it seem probable that the quality of ductility of solid silver could be here brought into play, for there is apparently no force which could be supposed to cause a drawing out of the metal. Hampe's explanation, that by being forced out through pores in a solidified and contracting crust, covering a fused interior, copper may have been caused to assume the wire form, cannot apply to silver, for the process here is undoubtedly a gradual one, the sulphide passing without fusion, as reduction occurs, into the form of pure silver wires. The results obtained in laboratory experiments suggest an explanation of one mode of occurrence of native metals in veins.

The wire silver found at Zacatecas, in Mexico, may have originated from reactions of such a character.

Hausmann (*Eng. and Min. Jour.*, May 2, 1890) describes the occurrence near Breckinridge, Summit County, Colo., of native gold possessing the remarkable wire-like forms, with fluted or grooved surfaces, so characteristic of silver and copper produced in the laboratory by the reduction of the sulphides by hydrogen.

The change into the fibrous condition at the temperature of

the puddling furnace, as cast-iron becomes converted by oxidation into puddled iron, may, perhaps, be considered similar to that which occurs in the reduction of silver sulphide by hydrogen.

The complete removal of impurities from the iron requires a temperature approaching fusion, and the fibers resulting as the metal becomes nearly pure are united into a mass.

THE PROTEIDS OF THE KIDNEY BEAN.

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

(Continued from page 643.)

Another portion of the bean-meal was extracted with a considerable quantity of one per cent. sodium chloride solution; the extract was filtered as clear as possible, and dialyzed in a large vessel containing alcohol. The globulin readily separated after a short time, in well-formed tetrahedral crystals mixed with amorphous matter. This precipitate was filtered off, treated for forty-eight hours with one per cent. sodium chloride solution, filtered clear and again precipitated by dialysis in alcohol, at first quite dilute, but afterwards of gradually increased strength. The substance now separated in large well-formed tetrahedral crystals, the edges of which were slightly curved. This precipitate was filtered off, washed with water, alcohol, and ether, dried and analyzed with results as follows:

PHASEOLIN, PREPARATION 18. CRYSTALS.

| | I. | II. | Average. | Ash-free. |
|---------------|-------|-------|----------|-----------|
| Carbon..... | 50.98 | | 50.98 | 52.70 |
| Hydrogen..... | 6.56 | | 6.56 | 6.78 |
| Nitrogen..... | 16.21 | 16.10 | 16.16 | 16.71 |
| Sulphur..... | 0.33 | 0.29 | 0.31 | 0.32 |
| Oxygen..... | | | | 23.49 |
| Ash..... | 3.27 | | 3.27 | |
| | | | | 100.00 |

As dilute acids precipitate proteid substance when added to the sodium chloride extracts of the ground beans, it was thought desirable to make some preparations by this method. Accordingly an extract was prepared by treating the meal with one per cent. sodium chloride solution, and after clearing as completely

as possible by subsidence and decantation, two-tenths per cent. hydrochloric acid was added until a considerable precipitate resulted. After standing some hours the precipitate was filtered off, dissolved in very dilute brine, filtered clear and precipitated by dilution. Only a small part of the substance separated. This preparation, 19, was then washed with water, alcohol and ether, dried and found to contain ash-free, 16.71 per cent. of nitrogen.

The filtrate from 19, when greatly diluted, gave a further precipitate, which, when filtered off and washed with water, alcohol and ether had the following composition:

PHASEOLIN, PREPARATION 20.

| | | Ash-free. |
|----------------|-------|-----------|
| Carbon | 51.85 | 52.20 |
| Hydrogen | 6.91 | 6.95 |
| Nitrogen | 16.15 | 16.26 |
| Sulphur | 0.51 | 0.51 |
| Oxygen | | 24.08 |
| Ash | 0.68 | |
| | | <hr/> |
| | | 100.00 |

It is evident that the same globulin was obtained by this method as by those previously followed. Next to be noticed are two preparations of phaseolin, made by diluting the sodium chloride extracts in the manner already described, redissolving the precipitates first obtained in salt solution, and again precipitating by dilution. Preparation 21, contained ash-free 16.65 per cent. of nitrogen.

PHASEOLIN, PREPARATION 22.

| | I. | II. | Average. | Ash-free. |
|----------------|-------|-------|----------|-----------|
| Carbon | 52.24 | | 52.24 | 52.55 |
| Hydrogen | 6.86 | | 6.86 | 6.90 |
| Nitrogen | 16.03 | 16.06 | 16.05 | 16.14 |
| Sulphur | 0.58 | | 0.58 | 0.58 |
| Oxygen | | | | 23.83 |
| Ash | 0.58 | | 0.58 | |
| | | | | <hr/> |
| | | | | 100.00 |

The filtrate from 22 was then treated with two-tenths per cent. hydrochloric acid, until a considerable precipitate resulted. This was filtered off, washed with water, alcohol and ether, and analyzed with the following results:

PHASEOLIN, PREPARATION 23.

| | | Ash-free. |
|----------------|-------|-----------|
| Carbon | 51.34 | 52.12 |
| Hydrogen | 6.59 | 6.70 |
| Nitrogen | 15.96 | 16.21 |
| Sulphur | 0.58 | 0.59 |
| Oxygen | | 24.38 |
| Ash | 1.48 | |
| | | 100.00 |

One more preparation of this globulin was made with special reference to its purity. For this purpose a considerable quantity of the globulin was precipitated from a one per cent sodium chloride extract of the beans, and after filtering off, was twice dissolved in dilute sodium chloride solution and precipitated by dilution after filtering clear. The final precipitate was thoroughly washed with water, alcohol and ether and analyzed. When dried over sulphuric acid, the preparation was readily soluble in dilute sodium chloride solution, and consisted entirely of the unaltered phaseolin. Its composition is shown by the analysis of preparation 24.

PHASEOLIN, PREPARATION 24.

| | I. | II. | Average. | Ash-free. |
|----------------|-------|-------|----------|-----------|
| Carbon | 52.45 | 52.52 | 52.49 | 52.75 |
| Hydrogen | 6.99 | 6.80 | 6.90 | 6.95 |
| Nitrogen | 16.52 | 16.39 | 16.46 | 16.57 |
| Sulphur | 0.56 | 0.44 | 0.50 | 0.50 |
| Oxygen | | | | 23.23 |
| Ash | 0.69 | | 0.69 | |
| | | | | 100.00 |

The properties of phaseolin as shown by careful examination of preparation 24, dried over sulphuric acid, are as follows:

In cold or warm distilled water it is entirely insoluble.

In sodium chloride solution, and in very dilute acids and alkalies, it is very readily soluble to a clear solution.

Dissolved in ten per cent. sodium chloride solution, it is not precipitated by acetic, hydrochloric, nitric, or sulphuric acids, added in either minute or considerable quantities, although when dilute hydrochloric acid is added to the one per cent. sodium chloride extract of the beans, the phaseolin is precipitated.

Dissolved in large proportion in ten per cent. sodium chloride solution, the proteid is precipitated by adding much pure water.

Solutions of phaseolin in brine are completely precipitated by saturation with ammonium sulphate, but only slightly by saturation with magnesium sulphate or sodium chloride.

Potassium ferrocyanide and acetic acid together, give a precipitate.

With copper sulphate and caustic potash, the usual violet coloration is obtained, and with nitric acid, the xanthoproteic reaction.

Dissolved in ten per cent. sodium chloride solution and heated very slowly in a double water-bath, no turbidity occurs until the temperature is raised to 95°. This turbidity slowly increases as the temperature approaches 100° and after some time, a flocculent precipitate begins to develop, which even after heating for an hour is but slight.

Like other plant-globulins, phaseolin separates from warm concentrated solutions on cooling, and from salt solutions on dialysis, in the form of spheroids.

The striking resemblance in composition of this proteid to the "myosins" found in the seeds of maize and oats, and also to animal myosin, is shown in the following table:

| | Phaseolin. | Maize
myosin. ¹ | Oat
myosin. ² | Animal
myosin. ³ |
|----------------|------------|-------------------------------|-----------------------------|--------------------------------|
| Carbon..... | 52.58 | 52.68 | 52.34 | 52.82 |
| Hydrogen | 6.84 | 7.02 | 7.21 | 7.11 |
| Nitrogen | 16.48 | 16.82 | 16.88 | 16.77 |
| Sulphur..... | 0.56 | 1.30 | 0.88 | 1.27 |
| Oxygen | 23.54 | 22.18 | 22.69 | 21.93 |
| | 100.00 | 100.00 | 100.00 | 100.00 |

The four proteids, although having many properties in common, as well as a similar composition, are yet characterized by differences so considerable, as to leave no doubt of the individuality of each.

The maize myosin and animal myosin differ from the other two, by their greater content of sulphur, and also in coagulating, the former at 70° and the latter at 55° C.

Phaseolin presents many points of difference from the oat myosin. It is not precipitated from solutions in ten per cent.

¹ *Am. Chem. J.*, 13, 536.

² Report Connecticut Agricultural Experiment Station for 1890, 137-160; also *Am. Chem. J.*, 13, 389; also Report Connecticut Agricultural Experiment Station for 1891, 135.

³ Studies from Laboratory of Physiological Chemistry, Yale University, 3, 133.

sodium chloride by acids, and but slightly by saturation with sodium chloride, and is thrown down, both by dilution and by dialysis, with much greater difficulty than the oat myosin.

SUMMARY OF ANALYSIS OF PHASEOLIN FROM THE KIDNEY BEAN.

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|--------------|--------|---------|--------|--------|--------|--------------------|----------|-------------------|------------------|
| Carbon..... | 52.23 | 52.60 | 52.60 | | 52.54 | | | 52.72 | 52.35 |
| Hydrogen... | 6.95 | 6.69 | 6.72 | | 6.83 | | | 7.24 ¹ | 6.89 |
| Nitrogen.... | 16.37 | 16.56 | 16.17 | 16.12 | 16.48 | 16.23 | 16.87 | 16.45 | 16.52 |
| Sulphur | 0.62 | 0.63 | 0.63 | | 0.58 | | | 0.67 | } 24.24 |
| Oxygen..... | 23.83 | 23.52 | 23.88 | | 23.57 | | | 22.92 | |
| | 100.00 | 100.00 | 100.00 | | 100.00 | | | 100.00 | 100.00 |
| | 10. | 11. | 12. | 13. | 14. | 15. | 16. | 17. | 18. ² |
| Carbon..... | 52.74 | 52.49 | | 53.06 | 52.49 | 52.47 | 53.22 | | 52.70 |
| Hydrogen... | 6.84 | 6.80 | | 6.85 | 6.73 | 6.90 | 6.86 | | 6.78 |
| Nitrogen.... | 16.65 | 16.85 | 16.67 | 16.68 | 16.45 | 16.00 ¹ | 16.48 | 16.29 | 16.71 |
| Sulphur | 0.64 | } 23.86 | | 23.41 | 24.13 | 24.63 | { 0.48 | | 0.32 |
| Oxygen..... | 23.13 | | | | | | | | |
| | 100.00 | 100.00 | | 100.00 | 100.00 | 100.00 | 100.00 | | 100.00 |
| | 19. | 20. | 21. | 22. | 23. | 24. | Average. | Rithausen. | |
| Carbon..... | | 52.20 | | 52.55 | 52.12 | 52.75 | 52.58 | 52.55 | |
| Hydrogen... | | 6.95 | | 6.90 | 6.70 | 6.95 | 6.84 | 7.09 | |
| Nitrogen.... | 16.71 | 16.26 | 16.65 | 16.14 | 16.21 | 16.57 | 16.48 | 16.18 | |
| Sulphur | | 0.51 | | 0.58 | 0.59 | 0.50 | 0.56 | 0.43 | |
| Oxygen..... | | 24.08 | | 23.83 | 24.38 | 23.23 | 23.54 | 23.75 | |
| | | 100.00 | | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | |

PREPARATION OF PHASELIN.

Proteid Remaining in Solution after Separation of the Globulin Just Described.

After precipitating phaseolin by the various methods employed in making the foregoing preparations, the extracts contained proteid matter which could be separated by dialysis in distilled water, by adding acids and by prolonged heating.

These methods of precipitation gave products of nearly uniform composition, except in those cases where the phaseolin had been incompletely separated. Preparations of phaselin were accordingly made as follows:

When a portion of the dialyzed solution from which preparation 1 had been separated, was heated slowly it became turbid

¹ Omitted in making average.² Tetrahedral crystals.

at 40°, flocks appearing at 68° in considerable quantity. When filtered, after heating at 72°, a second turbidity was obtained at 83°, and flocks formed at 87° in greater quantity than at 68°. The remaining solution was dialyzed in alcohol until its volume was reduced by one-half. An equal bulk of strong alcohol was then added to the contents of the dialyzer, and the mixture allowed to stand until the precipitate settled. After three days the solution was decanted and the precipitate washed with absolute alcohol and ether and dried over sulphuric acid. The substance, thus dried, weighed eleven grams. It was finely ground, thoroughly extracted with distilled water, and this extract filtered from the large insoluble residue. The clear solution was then found to become turbid when heated to 63° and to yield a flocculent coagulum at 76°. The entire solution was therefore heated for several hours in a water-bath at 80°, and the coagulum filtered off, washed thoroughly with water, alcohol and ether and dried over sulphuric acid. The 0.9 gram of substance thus obtained, was dried at 110° and analyzed with the following result. Preparation 25.

PHASKLIN, PREPARATION 25.

| | | Ash-free. |
|-----------------|-------|--------------|
| Carbon | 51.67 | 51.96 |
| Hydrogen | 6.67 | 6.71 |
| Nitrogen | 15.55 | 15.65 |
| Sulphur } | | 25.70 |
| Oxygen } | | |
| Ash | 0.57 | |
| | | <hr/> 100.00 |

When the filtrate from 25 was again heated to 80°, a further coagulum resulted. The solution was accordingly kept at this temperature as long as any coagulum was produced, filtered, and the coagulum washed with hot water, alcohol, and ether, and dried for analysis at 110°. This preparation, 26, contained, ash-free, 14.57 per cent. of nitrogen and weighed 0.71 gram.

Two other preparations were made from the filtrate from preparation 3, in nearly the same way as the two last described, the only difference being that the solution was precipitated with alcohol without first concentrating by dialysis in alcohol.

The first coagulum, preparation 27, obtained by heating at

80°, weighed only 0.17 gram, and when dry contained without correction for ash, 14.90 per cent. of nitrogen. The second weighed one gram and had the following composition:

PHASELIN, PREPARATION 28.

| | | Ash-free. |
|-----------------|-------|--------------|
| Carbon | 51.19 | 51.57 |
| Hydrogen | 6.87 | 6.92 |
| Nitrogen | 14.36 | 14.48 |
| Sulphur } | | 27.03 |
| Oxygen } | | |
| Ash | 0.75 | |
| | | <hr/> 100.00 |

After largely diluting, the filtrate from preparation 16 failed to give any further precipitate on passing carbon dioxide through it for some time. The greater part of this solution was then thrown away, but by chance a little acetic acid was added to the remainder and found to produce a precipitate. This precipitate was filtered off, washed with water, alcohol, and ether, and when dried, weighed 0.27 gram and contained without correction for ash, 14.81 per cent. of nitrogen. Preparation 29.

Another preparation was then made by extracting bean meal with one per cent. brine, diluting the extract with a large quantity of water, and filtering off the precipitate. The filtrate was then treated with two-tenths per cent. hydrochloric acid until a considerable precipitate resulted, which was filtered off and the solution again treated with two-tenths per cent. hydrochloric acid. This final precipitate was filtered off, washed with alcohol and ether and gave one gram of preparation 30, having the following composition:

PHASELIN, PREPARATION 30.

| | | Ash-free. |
|-----------------|-------|--------------|
| Carbon | 50.18 | 51.38 |
| Hydrogen | 6.53 | 6.71 |
| Nitrogen | 14.44 | 14.84 |
| Sulphur } | | 26.87 |
| Oxygen } | | |
| Ash | 2.74 | |
| | | <hr/> 100.00 |

Again, the filtrate from preparation 10, was treated with an equal volume of strong alcohol and allowed to stand over night.

The next morning, the precipitate which had separated was filtered off and treated with water. This dissolved some of the substance. This solution, filtered clear, when heated, gave a flocculent coagulum at 80°. With acetic, hydrochloric, or nitric acid, it gave a precipitate when the reagents were added in sufficient quantity. These precipitates were soluble in sodium chloride solution, and those produced by hydrochloric and nitric acids, were soluble in an excess of the acid, but that given by acetic acid, was not noticeably soluble in an excess. The precipitate obtained with nitric acid, did not dissolve upon warming, as is the case with such precipitates yielded by proteoses. The reaction of the extract was slightly acid, but it was not possible to precipitate anything therefrom, by the most careful neutralization. The whole solution was then treated with two-tenths per cent. hydrochloric acid; the precipitate thus formed had the following composition:

PHASELIN, PREPARATION 31.

| | | Ash-free. |
|-----------------|-------|-----------|
| Carbon | 49.91 | 51.98 |
| Hydrogen | 6.55 | 6.82 |
| Nitrogen | 13.95 | 14.53 |
| Sulphur } | | 26.68 |
| Oxygen } | | |
| Ash | 4.00 | |
| | | 100.00 |

The precipitate from which 31 was derived, after this extraction with water, was but slightly soluble in sodium chloride solution, and was therefore treated with two-tenths per cent. potash water. The resulting solution was filtered clear, and hydrochloric acid cautiously added, until a precipitate formed which was collected on a filter and treated in the usual manner. When dry, this preparation, 32, weighed 3.3 grams.

The filtrate from 32 was further treated with two-tenths per cent. hydrochloric acid, and a second precipitate obtained which weighed 0.6 gram; preparation 33.

PHASELIN, PREPARATION 32.

| | I. | II. | Average. | Ash-free. |
|----------------|-------|-------|----------|-----------|
| Carbon..... | 51.74 | 51.74 | 51.74 | 52.65 |
| Hydrogen | 7.04 | 7.00 | 7.02 | 7.14 |
| Nitrogen | 14.89 | | 14.89 | 15.15 |

| | I. | II. | Average. | Ash-free. |
|-----------------|------|------|----------|-----------|
| Sulphur } | | | | 25.06 |
| Oxygen } | | | | |
| Ash | 1.78 | | 1.78 | |
| | | | | 100.00 |

PHASELIN, PREPARATION 33.

| | | Ash-free. |
|----------------|-------|-----------|
| Nitrogen | 14.24 | 14.85 |
| Ash | 4.12 | |

Another preparation was made by extracting 100 grams of bean meal, with 100 cc. of one per cent. sodium chloride solution, and washing the insoluble residue with 100 cc. of the same solution, applied in successive portions. The entire extract was then filtered nearly clear, and dialyzed in alcohol. The alcohol of the outer vessel was frequently renewed, and the process was continued until practically all the proteid matter had separated. The precipitate was then filtered off and extracted with one per cent. sodium chloride solution. Much of the substance remained undissolved. The solution was filtered clear and dialyzed again in alcohol of 0.85 sp. gr. which was renewed once during the process. The precipitate resulting was filtered off and washed with dilute alcohol, absolute alcohol and ether and dried at 110°. Its composition was as follows:

PHASELIN, PREPARATION 34.

| | | Ash-free. |
|-----------------|-------|-----------|
| Carbon | 46.49 | 51.38 |
| Hydrogen | 6.25 | 6.91 |
| Nitrogen | 13.27 | 14.67 |
| Sulphur } | | 27.04 |
| Oxygen } | | |
| Ash | 9.53 | |
| | | 100.00 |

In order to obtain a purer preparation of the proteid by this method, 200 grams of bean meal, first extracted with petroleum-benzine, were treated with one liter of one per cent. sodium chloride solution and after squeezing out, the residue was mixed with another liter of the same solution and again squeezed. After standing over night, the turbid extract was decanted and dialyzed in alcohol for three days, the alcohol being once renewed. This treatment precipitated nearly all the proteids, which were

collected on a filter, and after the solution had run off, the precipitate was suspended in one-quarter per cent. sodium chloride solution, filtered off and washed with the same solution. The clear filtrate and washings were then dialyzed into alcohol until a considerable precipitate had formed which was filtered off and washed successively with fifty per cent. alcohol, stronger alcohol, absolute alcohol, and ether, and dried over sulphuric acid. It was then almost wholly soluble in water, but after drying at 110° it became insoluble, and was washed with water, alcohol, and ether, and again dried, 35.

PHASELIN, PREPARATION 35.

| | I. | II. | Average. | Ash-free. |
|-----------------|-------|-------|----------|-----------|
| Carbon..... | 49.01 | | 49.01 | 51.37 |
| Hydrogen | 6.77 | | 6.77 | 7.10 |
| Nitrogen | 14.26 | 13.82 | 14.04 | 14.71 |
| Sulphur } | | | | 26.82 |
| Oxygen } | | | | |
| Ash | 4.58 | | 4.58 | |
| | | | | 100.00 |

[TO BE CONTINUED.]

THE DETERMINATION OF ALBUMEN IN COW'S MILK.

BY L. L. VAN SLYKE.

Received August 22, 1894.

IN Vol. 15, No. 11 of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, the writer presented a paper on the determination of casein in cow's milk. It is now desired to present another paper supplementary to that and relating to the determination of albumen in cow's milk.

Ordinarily, when we speak of milk albumen, we mean the portion of nitrogen compounds not coagulated by rennet, acid, etc. In other words, we apply the term albumen to the nitrogen compounds left after removing the casein proper. This use of the term albumen is inaccurate, because, after removing from normal milk its casein, there remain, at least, two nitrogen compounds or classes of nitrogen compounds. One of these is coagulated by heat, especially in the presence of dilute acids, while the other is not coagulated under these conditions. To the former only of these two, the term albumen is properly applicable.

DETAILS OF METHOD.

The filtrate obtained, after separating the casein by the method described in the article above referred to, is placed in a water-bath heated to the boiling temperature of water, the beaker containing the filtrate being covered with a watch-glass crystal. The solution is kept at this temperature until the albumen coagulates and settles to the bottom, leaving the supernatant liquid clear. Ten or fifteen minutes usually suffices to accomplish this. The precipitate is filtered, washed and then treated according to the Kjeldahl method for determining nitrogen. The amount of nitrogen multiplied by the factor 6.25 gives the amount of albumen.

It was thought that too long boiling of the albumen precipitate might cause some of it to redissolve; and, in order to ascertain what effect the length of time of heating influenced the results, the digestion was varied from five minutes to ten hours. The tabulated results are as follows:

| No. of sample
of milk. | Length of time solution containing albumen was heated. | | | | | | | | | |
|---------------------------|--|---------------------|---------------------|---------------------|---------------------|---------------------|----------|-----------|-----------|------------|
| | 5
Min-
utes. | 10
Min-
utes. | 15
Min-
utes. | 20
Min-
utes. | 30
Min-
utes. | 45
Min-
utes. | 1
Hr. | 2
Hrs. | 4
Hrs. | 10
Hrs. |
| | Per cent. of nitrogen in albumen contained in milk. | | | | | | | | | |
| 1..... a { | 0.060 | | 0.057 | 0.054 | 0.056 | 0.057 | 0.061 | 0.046 | 0.060 | |
| "..... b { | 0.062 | 0.058 | 0.048 | 0.051 | 0.063 | 0.062 | 0.059 | 0.055 | 0.054 | |
| "..... Average | 0.061 | 0.058 | 0.053 | 0.053 | 0.059 | 0.059 | 0.060 | 0.051 | 0.057 | |
| 2..... a { | 0.014 | 0.054 | 0.054 | 0.052 | 0.052 | 0.051 | 0.052 | 0.047 | 0.045 | |
| "..... b { | 0.044 | 0.053 | | 0.054 | 0.051 | | 0.051 | 0.051 | 0.049 | |
| "..... Average.. | 0.029 | 0.053 | 0.054 | 0.053 | 0.052 | 0.051 | 0.051 | 0.049 | 0.047 | |
| 3..... a { | 0.054 | 0.053 | 0.049 | 0.052 | 0.051 | 0.053 | 0.057 | 0.057 | 0.056 | 0.058 |
| "..... b { | 0.054 | 0.047 | 0.053 | 0.056 | | 0.057 | 0.057 | 0.060 | 0.053 | 0.055 |
| "..... Average.. | 0.054 | 0.050 | 0.051 | 0.054 | 0.051 | 0.055 | 0.057 | 0.058 | 0.055 | 0.056 |
| 4..... a { | 0.057 | 0.064 | 0.061 | 0.061 | 0.065 | 0.065 | 0.062 | 0.062 | 0.069 | 0.065 |
| "..... b { | 0.062 | 0.055 | 0.065 | 0.063 | 0.064 | 0.062 | 0.065 | 0.066 | | 0.065 |
| "..... Average.. | 0.059 | 0.060 | 0.063 | 0.062 | 0.064 | 0.063 | 0.063 | 0.064 | 0.069 | 0.065 |
| Average of all results.. | 0.047 | 0.056 | 0.056 | 0.055 | 0.055 | 0.057 | 0.057 | 0.058 | 0.056 | 0.059 |

An examination of the foregoing table shows:

- (1) In one case, heating for five minutes gave low results; in two other cases, good results.
- (2) In general, the results varied little with increased length of time of heating.
- (3) There was a slight tendency to higher results with

increased length of heating, but such increase was more or less irregular and, at most, amounted to only 0.002 or 0.003 per cent. of nitrogen.

(4) It would, therefore, appear that entirely satisfactory results can be obtained by heating the solution containing albumen under the given conditions for ten or fifteen minutes, while an increased length of time of heating does not practically change the results.

It may be stated that the precipitate formed always filters readily and washes easily.

SEPARATION AND DETERMINATION OF THE NITROGEN COMPOUNDS OF COW'S MILK.

Below we give a brief summary of our method as we employ it in effecting the determination and separation of the three classes of nitrogen compounds present in the normal milk of cows.

1. *Total Nitrogen Compounds*.—Determine the amount of total nitrogen by the Kjeldahl method and multiply by the factor 6.25.

2. *Casein*.—Weigh out about ten grams of milk, dilute in a beaker with about ninety cc. of water at 40°–42° C., and add at once 1.5 cc. of a solution containing ten per cent. of acetic acid, by weight. Stir with a glass rod and let stand three to five minutes longer. Then decant on a filter, wash two or three times with cold water by decantation and then transfer precipitate completely to filter. Wash once or twice on filter. The washed precipitate and filter paper are then digested as in the regular Kjeldahl method for the determination of nitrogen, and the determination completed in the usual manner. To calculate the nitrogen into an equivalent amount of casein, multiply the amount of nitrogen by the factor 6.25.

3. *Albumen*.—The filtrate obtained above in separating casein is placed in a water-bath and heated to the boiling temperature of water for ten or fifteen minutes. The filtered and washed precipitate is then treated by the Kjeldahl method for determining nitrogen. The amount of nitrogen multiplied by 6.25 gives the amount of albumen.

4. *Remaining Nitrogen Compounds*.—The remaining compound or compounds of nitrogen are determined by difference,

subtracting from the amount of total nitrogen compounds the sum of the casein and albumen.

In conclusion, I wish to call attention to the crude nomenclature in common use in stating the results of milk analysis for nitrogen compounds. It is an almost universal custom to call the total nitrogen compounds of milk casein. It would be quite as correct to call the fat of milk palmitin or some similar name. This wrong use of the term casein leads to much confusion, and it is highly desirable that we should use a more discriminating nomenclature. It is also desirable that, in making analysis of milk, pains should be taken to separate and determine the different kinds of nitrogen compounds, since our knowledge of these compounds is far from complete.

I am much indebted to Mr. A. L. Knisely for assistance rendered by him in carrying out the analytical details of the work.

AN APPARATUS ("LYSIMETER") FOR DETERMINING SOLUBILITIES.

BY CHARLES RICE.

Received July 11, 1894.

IN determining the solubility of a substance in some liquid at a given temperature, there is usually but little difficulty encountered when the solvent is not very volatile and the temperature at which the determination is to be made is not high. With a highly volatile solvent, and a high temperature, however, certain difficulties present themselves which are liable to lead to error. The main difficulty is encountered in the endeavor to separate from the original solution, which usually contains an excess of the substance in suspension, a *filtered* portion at the same temperature as that of the solution. The higher this temperature is, the more difficult becomes the removal of a portion without the introduction of errors by the ordinary methods of filtration. It appears, therefore, that it is only necessary to modify the method of filtration in such a way as to maintain the temperature of the original solution unchanged in order to eliminate these errors. This may be easily accomplished by upward filtration into a tube placed in the original solution, and so constructed that it will enable the operator to control the act of filtration, as well as accurately to determine the amount of solvent

and dissolved material. For this purpose the little apparatus here described has been found very serviceable.



The apparatus consists of a glass tube *a*, fifteen cm. long and one cm. in external diameter, provided at one end with a well-ground stopper *c*, while the other end is cup-shaped, there being a contracted neck between the cup and the main tube. Into this cup is made to fit, a carefully ground glass bell *e*, having a perforation in its bottom (as shown in *f*). There is also a stopper *b* which is carefully ground to fit into the cup, and which is inserted after the glass bell *e* has been removed. The several stoppers, etc., are all numbered to show where they belong.

To show how the apparatus is used it will be best to quote a practical example.

Let us assume that the solubility of morphine in boiling alcohol is to be determined. It will be necessary to provide for such an amount of liquid that at least one-half of the glass tube *a* may be immersed in the liquid. In the case of comparatively cheap solvents and substances to be dissolved, beaker glasses may be used; for more expensive materials, test-tubes of such a size that there will be no great waste of material are preferable.

The glass tube is made ready by inserting the stopper *c*, and introducing into the cup-shaped end the glass bell *e*, containing a pellet of purified cotton and prevented from dropping out by a thin platinum wire fastened around the contracted neck and crossed over the mouth of the bell. A sufficient amount of alcohol having been introduced into a beaker, or test-tube, heat is applied and morphine added until, after the boiling has been kept up some time, a portion of the alkaloid remains

undissolved. The prepared glass tube is now inserted in the liquid. As long as the stopper *c* closes the mouth of the tube no liquid will be able to filter upwards. When the tube has acquired the temperature of the boiling liquid the stopper *c* is removed, whereupon the liquid will begin to filter through the pellet of cotton and rise in the tube as far as the quantity of liquid will permit. In order to insure perfect uniformity of the liquid within and without the tube, it is best to allow the filtered portion to flow back through the pellet of cotton once or several times. The stopper *c* having then been inserted, the tube is withdrawn, turned upside down, the glass bell removed, and the stopper *b* inserted. The tube is now carefully cleaned with alcohol, and laid aside until cold. Its tare having previously been determined, the increase in weight represents the weight of the solution contained therein. On transferring or washing the contents into a tared beaker or capsule and evaporating, the weight of the dissolved morphine will be found.

The apparatus here described, which has been frequently in use during several years, and to which, for brevity's sake, the name *lysimeter* (from the Greek *lysis*, solution) has been given, was made for the writer in a very satisfactory manner by Mr. Emil Greiner, of New York City.

NEW YORK, July 7, 1894.

NEW BOOKS.

THE DECOMPOSITION OF THE FIXED ALKALIES AND ALKALINE EARTHS.

By Humphry Davy, 1807-1808. Alembic Club Reprint, No. 6. 12 mo. 51 pp. Edinburgh: William F. Clay. 1894.

This number of the Alembic Club Reprints contains the Bakerian Lecture delivered by Davy before the Royal Society in 1807, and also part of a paper communicated by him to the same Society in the following year. The Bakerian Lecture is on the Decomposition of the Fixed Alkalies and on the General Nature of the Alkaline Bodies. The other paper is on the Decomposition of the Earths, with observations on the metals obtained from the alkaline earths.

In the first paper we have the first published record of the experiments by which Davy proved the compound nature of the alkalies and prepared the metals potassium and sodium. The

second paper contains a description of similar experiments upon the earths and alkaline earths, only that part which deals with the successful experiments being reprinted. W. R. O.

THE DISCOVERY OF OXYGEN. By Joseph Priestley, 1775, and Carl Wilhelm Scheele, 1777. Being Nos. 7 and 8 of Alembic Club Reprints. Edinburgh: William F. Clay. 1894.

Among the first things learned by students in chemistry, is that "oxygen was discovered almost simultaneously by Priestley in England, in 1774, and Scheele, in Sweden, in 1775." That the work of these men was independent of each other is also well known. Many have become acquainted with their work in a general way, but few have had the opportunity of following the original experiments as described by the experimenters. This opportunity is offered now by the publishers of the Alembic Club Reprints. Nos. 7 and 8 of this series are the Discovery of Oxygen. Part I (No. 7) by Joseph Priestley, and Part II (No. 8) by Carl Wilhelm Scheele, the latter a translation. They consist of sections taken from larger works of these authors, and, save for a short preface by the publisher, are without note or comment. Both Priestley and Scheele are minute in the description of the numerous experiments carried out in this work.

They began experimenting at different ends of the subject. Priestley was of the "try something" type of worker, and in his different experiments the peculiarities of "dephlogisticated air," as he afterwards called it, "obtruded themselves upon him." He first obtained the "air" then studied its properties. He tried to obtain this "air" from every available substance. The bulk of it was obtained from mercuric oxide and red lead and nitric acid. Scheele, on the other hand, found that air was not a simple substance, but contained a gas, which he called "fire air." The experiments which were performed when this truth was discovered are well described. They consisted in placing oxidizable substances in bottles which were well corked, and allowing the air in them to act for different periods of time, then opening the bottles under water and noting the diminution in the volume of air by the water entering the bottles. Then the work of producing "fire air" was undertaken, numerous experiments were carried out, the results of which are well known.

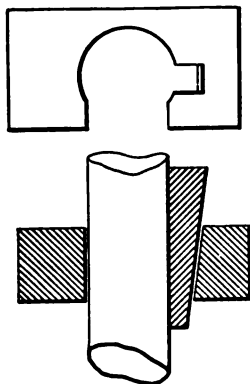
These two men had the theory of combustion in their grasp, and almost explain it in their writings, that they were unconscious of this fact is surprising.

The publishers of these Reprints are to be thanked for placing before the chemical world the work of these two men in such a handy and attractive form. A digest of a work is good, but the original furnishes the only true satisfaction. So these little books should be extremely valuable to the student, by enabling him to see the discovery of oxygen in its original shape.

OWEN L. SHINN.

NOTES.

Convenient Burette Clamp.—A convenient form of burette holder may be made from the appended sketch. A simple wedge being employed in place of the screw clamp to hold the tube in position. The surface of the wedge bearing on the tube should be slightly curved to ensure accurate contact. Cork is not necessary on bearing parts, as very slight pressure on upper end of wedge causes the tube to be held with great rigidity. Holder should be made of maple, wedge of hickory or other hard wood. — *Clarence Quinan.*



A New Atmospheric Element.—Lord Rayleigh and Professor Ramsay announce the discovery of a supposed new element contained in the atmosphere to the extent of about one per cent. Two methods of separation have been used. The first method consists in passing high tension electrical sparks through a mixture of equal bulks of air and oxygen confined over potash solution until no further diminution in volume ensues. The excess of oxygen is then absorbed by alkaline pyrogallate. The second method consists in removing the oxygen from air by red hot copper and the nitrogen by heated magnesium. The remaining gas has a sp. gr. of 18.9 and is more inert than nitrogen.

Wm. Crookes has examined the spectrum of the gas when the

induction spark is passed through a tube containing the new gas under an exhaustion of eight mm., and finds that "the spectrum is a very definite and characteristic one, and the lines differ in position from those of nitrogen. The appearance more resembles a metallic spectrum, and no flutings similar to those of nitrogen are to be seen." Professor Dewar suggests that the new element may be an allotropic form of nitrogen analogous to red phosphorus, and that the processes of preparation may be really methods of manufacture. E. H.

The Post-Mortem Detection and Estimation of Strychnine—Allerton S. Cushman. (*Transactions of the Academy of Science of St. Louis*, 6, 537.)

The author recommends the following method for the detection and estimation of strychnine in toxic cases: The mass to be examined is comminuted and digested over night at a warm temperature with water acidulated with acetic acid, filtered through muslin and then through paper, the solution evaporated, an excess of eighty per cent. alcohol added, boiled, filtered, and extraction repeated. The liquid is then evaporated, the residue taken up with water and a little acetic acid, and the solution shaken repeatedly with acetic ether, as long as anything is extracted—twelve extractions may be necessary. A volume of acetic ether equal to that of the solution is now added, and sodium carbonate to alkaline reaction. After shaking, the acetic ether is separated and the extraction repeated. The strychnine is usually moderately pure as obtained by the evaporation of the acetic ether, but for quantitative estimation it is dissolved in dilute acetic acid, filtered, the solution extracted with ether-chloroform (1:1), ammonia added, and the extraction with ether-chloroform repeated twice. The residue obtained by evaporating the ether-chloroform is nearly pure and is weighed. Two experiments with known amounts of strychnine mixed with considerable amounts of meat, sugar, starch, and water, and allowed to stand in a warm place for two weeks, gave a recovery of about eighty-seven per cent. of the strychnine present. Directions for chemical, crystallographic, and physiological tests are given. Two toxic cases in which the method was applied are also given.

W. A. NOYES.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE
UNIVERSITY.]

A METHOD FOR DETERMINING CALCIUM OXIDE IN QUICKLIME.

BY W. E. STONE AND F. C. SCHEUCH.

Received September 1, 1894.

THE value of quicklime is based upon the amount of calcium oxide which it contains. This value may be diminished by the presence of other substances originally present in the limestone, consisting usually of magnesia, alumina, silica, and iron; by incomplete ignition in the lime-kiln, on account of which some calcium carbonate fails to be converted into calcium oxide; and lastly, by a partial "slaking," by which a portion of the calcium oxide reverts to calcium carbonate.

An analysis of quicklime, therefore, should show not only the amount of calcium present in distinction from other elements, but should distinguish between the calcium as oxide and other forms of combination. The customary gravimetric method, based upon solution of the calcium compounds in acids, precipitation as calcium oxalate, ignition, etc., attains only the first of these requirements and affords no data for judging of the original condition of the calcium thus found. Consequently this method may furnish erroneous conclusions with regard to the commercial value of the material examined.

The method here proposed enables one to determine with a high degree of accuracy and rapidity the actual amount of calcium oxide in quicklime. It is based upon the well-known fact that

the alkaline earths form definite compounds with sucrose, called saccharates. Several such compounds are known with barium and strontium. With calcium oxide, sucrose forms at least three compounds, the mono-, di- and tricalcium saccharates, containing respectively one, two, and three molecules of calcium oxide to one of sucrose. The two first are formed when quicklime is dissolved in the cold in a sucrose solution. On heating this to boiling, a precipitate is thrown down consisting in the main of the tricalcium saccharate.

Numerous authorities may be quoted with regard to the solubility of calcium oxide in sucrose solutions of which the two following will suffice for citation.

Berthelot¹ gives the maximum solubility in solutions of sucrose of varying strength.

| | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|
| Grams sugar in 100 cc... | 0.096 | 0.400 | 1.058 | 1.386 | 2.000 | 4.850 |
| CaO dissolved..... | 0.154 | 0.194 | 0.281 | 0.326 | 0.433 | 1.031 |

The following data are from Schatten.²

In ten grams of sugar solution of different percentages:

| | | | | | |
|----------------------------|-------|-------|-------|-------|-----|
| Per cent..... | 1. | 4. | 8. | 12. | 16. |
| Grams CaO dissolved, 0.029 | 0.080 | 0.160 | 0.271 | 0.394 | |

Numerous other references indicate the ready solubility of calcium oxide in sucrose solutions, and the apparent possibility of applying this fact to the separation of the actual calcium oxide from the other constituents of quicklime, led us to make the following studies:

1. The conditions under which calcium oxide is dissolved in sucrose solutions:

Lamy³ has shown that solubility varies inversely with the temperature. Ten liters of ten per cent. sucrose solution, at the given temperatures, dissolved the stated amounts of calcium oxide.

| | | | | | | |
|--------------------------|-----|-----|-----|-----|-----|------|
| Temperature C°..... | 0° | 15° | 30° | 50° | 70° | 100° |
| Grams CaO dissolved..... | 250 | 215 | 120 | 53 | 23 | 15.5 |

For our experiments, pure calcium oxide was prepared by igniting pure calcium carbonate to a constant weight. It was

¹ *Ann. Chim. phys.*, [3], 46, 176.

² Von Lippmann, *Die Zucker-Arten*, 109.

³ *La Sucrierie indigene et Coloniale*, 11, 19.

found by repeated experiment that one gram of this material was easily soluble in 150 cc. of a ten per cent. sucrose solution after agitating fifteen to twenty minutes at ordinary temperature. To accomplish perfect solution it was necessary that the material be finely pulverized. If heat were employed, the lime was converted into a pasty, insoluble mass which, however, dissolved on cooling.

2. The degree of solubility of calcium oxide in sucrose solution. Repeated experiments gave the following results:

One gram of pure CaO was only partly dissolved in 100 cc. of a five per cent. sugar solution.

One gram of pure CaO was only partly dissolved in 150 cc. of a five per cent. sugar solution.

One gram of pure CaO was only partly dissolved in 100 cc. of a ten per cent. sugar solution.

One gram of pure CaO was completely dissolved in 150 cc. of a ten per cent. sugar solution.

From these results it appears that not less than 150 cc. of a ten per cent. solution of sucrose could be safely employed to dissolve the calcium oxide in one gram of quicklime.

3. Behavior of other constituents of quicklime toward sucrose solutions:

Besides calcium oxide, quicklime usually contains more or less iron, alumina, magnesia, and silica. In addition to these, calcium carbonate may also be present. The behavior of these toward sucrose solutions was studied in detail with the following results:

Magnesia. Pure magnesium oxide, specially prepared, was treated with a ten per cent. solution of sucrose. One hundred and fifty cc. of the latter, after shaking with one gram of magnesium oxide for thirty minutes, were filtered and treated with ammonia and sodium phosphate, but only the faintest turbidity resulted. Again, one gram of magnesium oxide was shaken with 150 cc. of sucrose solution, filtered, and the filtrate titrated with standardized hydrochloric acid, and an equivalent of 0.001 gram of magnesia was found, or one-tenth of one per cent. These results show that magnesia is not appreciably soluble under the given conditions. Indeed, the existence of a com-

pound between magnesia and sucrose is doubted. On the other hand, magnesia is said to be freely soluble in a solution of calcium oxide in sucrose.¹ To test this point, mixtures of pure magnesium and calcium oxides were treated with sugar solutions as follows: One-half gram of each were mixed and shaken with 150 cc. of sugar solution. A considerable portion of the material was insoluble. We filtered and titrated the filtrate with standardized acid, the result being an exact equivalent of the calcium oxide employed. Again, one-half gram of each were mixed and treated with sugar solution as before. We filtered and precipitated the calcium from the filtrate by means of ammonium oxalate. The filtrate from this showed only slight turbidity when treated with ammonium and sodium phosphate. These results show that magnesium oxide is not soluble to an appreciable degree in sucrose solution containing calcium oxide, under the stated conditions.

Alumina was found quite insoluble, no appreciable amount being found in the filtered sucrose solution.

Calcium carbonate was also insoluble to any appreciable degree in the ten per cent. sucrose solution under the stated conditions.

Ferric oxide shaken with ten per cent. sugar solution was also insoluble. Schachtrup and Spunt² mention that ferric oxide inverts sucrose but not in an alkaline solution. We have verified this by heating a small quantity of ferric oxide with a sugar solution; the latter soon acquired the power of reducing Fehling's solution. But when the same experiment was repeated with the addition of some calcium oxide no inversion occurred. It is evident, therefore, that the iron contained in quicklime would not be affected by sucrose solution.

4. The determination of calcium oxide when dissolved in sucrose solution:

Calcium oxide when dissolved under the preceding conditions admits of determination, either gravimetrically by precipitation as calcium oxalate or volumetrically by titration with hydrochloric acid. Several comparisons of the two methods were made, using known amounts of pure calcium oxide and while

¹ Von Lippmann, *Die Zucker-Industrie*, 148.

² *Pharm. Cent. Hdlr.*, 34, 145.

each were accurate to the extent of yielding the theoretical numbers, the volumetric method was found preferable on account of its greater rapidity. For the latter method, standardized hydrochloric acid of about fifth-normal strength was employed, using tropaeolin or rosolic acid as an indicator.

5. Application of the preceding data to the analysis of quicklime.

Following the conclusions derived from the preceding tests, several samples of quicklime were analyzed for calcium oxide. They were all in a fresh state and contained little calcium carbonate.

In each case, approximately one gram of the finely pulverized material was shaken with 150 cc. of a ten per cent. sucrose solution during twenty minutes, the solution filtered and the clear filtrate titrated with standardized hydrochloric acid. At the same time other portions of the same samples were dissolved in hydrochloric acid and the calcium determined in the usual way by precipitation as calcium oxalate. Following are the results:

| Sample. | Weight of quicklime taken, grams. | Volume of ten per cent. solution of sucrose taken, cc. | Per cent. CaO by titration method. | Per cent. CaO by gravimetric method. | Variation of volumetric method. |
|-------------|-----------------------------------|--|------------------------------------|--------------------------------------|---------------------------------|
| No. 1 | 1.020 | 150 | 92.12 | 93.00 | —0.88 |
| " 2 | 1.090 | 150 | 91.90 | 92.28 | —0.38 |
| " 3 | 1.006 | 150 | 92.15 | 93.10 | —0.95 |
| " 4 | 1.108 | 150 | 95.01 | 95.90 | —0.89 |
| " 5 | 1.023 | 150 | 87.30 | 87.70 | —0.40 |
| " 6 | 1.232 | 150 | 91.70 | 92.30 | —0.60 |

The results by the sucrose method were in each case slightly lower than by the gravimetric method discrepancy which may be ascribed to a small amount of calcium carbonate present in the sample.

In quicklime which had become partially slaked, this discrepancy would be still greater since the sucrose method would indicate only the actual calcium oxide. Aside from this, the greater ease and rapidity of the latter recommends it in cases where the total calcium is present in the form of the oxide. An entire determination may thus be made in a half-hour with a degree of accuracy quite sufficient for all ordinary purposes.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE
UNIVERSITY.]

A COMPARISON OF METHODS FOR THE DETERMINA- TION OF STARCH.

BY W. E. STONE.

Received September 1, 1894.

THERE is no longer much doubt among chemists that, in food analysis, the present practice of classifying a large number of widely varying substances under the head of non-nitrogenous extract matter, as an homogeneous material, is wholly erroneous and misleading. The variety of substances covered by this term is well known, and, while it is granted that they are mainly of carbohydrate nature, it is equally clear that, so far as food valuation is concerned, there should be some degree of differentiation between sugars, starches, gums, and the more or less soluble forms of cellulose.

The position of the pentosans in this class of bodies has been pointed out in its different aspects by myself and others at intervals during the past four or five years. It has been shown that these bodies form a distinct constituent of the non-nitrogenous extract matter to a greater or less degree in all fodder articles; that under present analytical methods their individuality as food constituents is wholly merged into that of the more valued carbohydrates; some light has also been thrown upon their digestibility, and analytical methods of a fair degree of accuracy have been devised for their estimation in the presence of other similar bodies.

Mention is made of this instance here to show that really some progress has been made, and that too within a short time, in our knowledge of what, until recently, has been an obscure constituent of the non-nitrogenous extract matter.

The object of this present paper is to call attention along the same line to certain proposed methods for the quantitative estimation of probably the most important of these bodies; *viz.*, starch. At first thought it may appear that the existing methods for the determination of starch are sufficiently satisfactory and accurate; and this is, doubtless, true so far as starch alone is

concerned. But it must be remembered that starch almost always occurs in connection with other soluble non-nitrogenous matters, under which conditions its estimation becomes quite another matter and constitutes exactly the question under discussion. The pentosans or gums are, doubtless, the most common of these accompanying substances and, unfortunately for the analyst, behave toward many analytical methods precisely like starch. Hence, a result which is interpreted to mean starch by a strict adherence to the method, may be due, to a very large degree, to other substances. For example, brewers' grains, which from the very process through which they have passed contain little or no starch, will by the ordinary method of inversion and titration be credited with a large amount of starch. Again, hay or straw yield considerable amounts of reducing sugars on inversion, although they contain a minimum of starch, or even none at all. In both these cases the results are due to the inversion of insoluble gums which are present in large quantities.

With these facts in mind it is apparent that a food analysis should give some information with regard to the relative amounts of these different substances present, and should include determinations of the pentosans, sugars, and starches separately.

In this connection the inquiry arises as to how accurately it is possible to determine these bodies as they occur in connection with each other in the ordinary feeding stuffs, by current and accepted methods. As regards the pentosans and sugars, the state of our knowledge seems far more satisfactory than in the case of the starches, in proof of which proposition the following data are offered.

Five methods of starch determination have been compared upon a variety of materials. Four of the methods involve the inversion of the starch and the estimation of the sugar thus formed by volumetric or optical methods; the fourth method is based upon a combination of the starch with one of the alkaline earths. Following are the details of the different methods:

1. Inversion of the starch with hydrochloric acid and titration with Fehling's solution, known as Sachsse's method: Three to five grams of the starch bearing material are heated in a water-bath with 200 cc. of water and twenty cc. of concentrated acid,

during three hours; the acid is neutralized with soda, the solution filled to 500 cc., and titrated with Fehling's solution in the usual manner.

2. Inversion with nitric acid and polarization, proposed by Guichard, *Bull. Soc. Chim.*, [3,] 7, 554: Three grams of the material are heated in a water-bath during one hour with 100 cc. of ten per cent. nitric acid, filled to 200 cc. and polarized. The readings are calculated to dextrose.

3. A modification of the preceding: Three grams of material are heated in the water-bath with 100 cc. of a saturated solution of oxalic acid during one hour, the object being to bring the starch into solution. The liquid is cooled and filled to 200 cc. with ten per cent. nitric acid, filtered, and the filtrate heated in the water-bath one hour, attached to an inverted condenser. The solution is then polarized. This method is preferable to the other in that the cellulose and other insoluble substances are removed from the influence of the nitric acid.

4. Inversion of the starch by salicylic acid and polarization, proposed by A. Baudry, *Zeit. f. Spiritus Industrie*, 15, 41, 42: A normal weight, 5.376 grams is adopted for the Laurent polariscope. This weight, or some multiple of it, is placed in a 200 cc. flask with 100 cc. of water and four-tenths to one-half gram of salicylic acid and heated in a water-bath for thirty minutes; fill to within twenty cc. of the mark with hot water, cool rapidly, clarify by adding a few drops of ammonia, filter and polarize in a 400 mm. tube. The readings on the percentage scale indicate percentages. In our practice, sodium hydroxide was used instead of ammonia for clarifying.

5. Precipitation of the starch from the condition of paste by barium hydroxide, and determination of the excess of the latter by titration with a standard acid, proposed by A. von Asboth, in 1887: One gram of the material, from which the fat has been extracted, is boiled with water to convert the starch into a paste; twenty-five cc. of a solution of barium hydroxide of known strength is run in and the whole allowed to cool; then add 100 cc. of eighty-five per cent. alcohol and fill to 200 cc. A compound of starch is formed containing 19.1 per cent. of barium oxide, which is precipitated by the dilute alcohol. The solution is fil-

tered and the excess of barium hydroxide is determined by titrating aliquot portions with standardized hydrochloric acid, using phenolphthalein as an indicator.

The materials to which these methods were applied included nine different samples, as follows: Pure potato starch, wheat bran, wheat middlings, wheat flour, dried potatoes, corn-meal, hay, cottonseed-meal, and a mixture of starch, sugar, and dextrine. Four of these were samples sent out by the reporter on feeding stuffs of the Association of Official Agricultural Chemists. Before examination, the samples were extracted with water and ether to remove soluble carbohydrates and fats.

The results obtained are best shown by tabulation, as follows:

| Materials. | Inversion
by HCl. | Inversion
by HNO ₃ . | Inversion
by oxalic
acid and
HNO ₃ . | Solution
by
salicylic
acid. | Precipitation by
Ba(OH) ₂ . |
|---|----------------------|------------------------------------|--|--------------------------------------|---|
| 1. Pure potato starch..... | 85.75 | 85.50 | 85.75 | 85.47 | 85.58 |
| 2. Dried potato..... | 70.92 | 69.79 | 68.53 | | 64.25 |
| 3. Wheat flour | 77.69 | 70.65 | 65.29 | 69.38 | 59.76 |
| 4. Corn-meal | 73.24 | 66.81 | 70.55 | | 62.11 |
| 5. Wheat bran..... | 65.86 | 40.25 | 38.68 | | 70.77 |
| 6. Hay | 3.48 | 19.10 | 19.10 | | 66.47 |
| 7. Wheat middlings..... | 30.00 | 63.09 | 60.24 | | 60.44 |
| 8. Cottonseed-meal | 4.15 |* |* | | 54.65 |
| 9. Mixture of starch, sugar,
and dextrine..... | 9.58 | 21.00 | 24.08 | 18.8 | 33.99 |

* These solutions were laevorotatory.

From a survey of these data it appears that any of the methods employed, give satisfactory results when dealing with starch alone. It is important to recognize this in order that the responsibility for the discrepancies in connection with the other materials may be properly placed where it belongs; *viz.*, that the variations are due to the complex nature of the materials and not to the method. Allowing for moisture and cellulose, the starch was pure and each method gave credit for the entire amount present. Turning to the other materials the following is to be noted.

1. Inversion by hydrochloric acid. The starch is converted into dextrose and under carefully controlled conditions the reaction is quantitative. Wohl has shown that a very small quantity of acid is efficient in producing complete inversion.

(*Ber. d. chem. Ges.*, **23**, 2084.) According to Märcker, the method of Sachsse here employed gives slightly low results owing to a slight destruction of dextrose by long heating with the acid. This objection does not appear here in comparison with the other methods. There is undoubtedly danger in the other extreme in not heating long enough. The samples numbered 6, 7, 8 and 9 were treated according to the directions sent out by the A. O. A. C. which call for the removal of heat as soon as the starch-iodine reaction disappears. It is possible that under these conditions which are accomplished in a very short time, an appreciable amount of starch does not pass beyond the dextrine stage and escapes detection by Fehling's solution. In this connection it is noticeable that the samples 6, 7, 8 and 9 treated in this way, gave lower results by this than by the other methods.

2. The methods calling for the use of nitric acid seem unusually destructive, yet in the case of pure starch they have given results fairly comparable with the others. As originally proposed by the author, it was feared that the cellulose would be attacked, and the use of oxalic acid as in the third method was proposed. This provides for the solution and removal of the starch by a comparatively mild reagent and this solution is then inverted by the nitric acid apart from the accompanying constituents of the material. The method has a certain advantage of ease and rapidity; the solutions obtained for polarization are also beautifully clear and admit of accurate readings. The effect of the direct action of the acid in the second method is not so marked as might be expected.

3. Both salicylic and benzoic acids completely dissolve starch; the solutions have a right-handed polarization and the degree of rotation is directly proportional to the amount of starch present. The method was originally proposed for the valuation of commercial starches and with such materials is fairly accurate. With feeding stuffs, however, the resulting solutions are frequently too highly colored and opaque to admit of examination in the polarimeter. The method is therefore of very limited application.

5. The use of barium hydroxide as a means of combining and

precipitating starch from solution has attractive features and has been both highly praised and severely criticised. It necessitates the previous removal of all oils from the material. In our hands the results obtained have been somewhat erratic.

One fact is apparent in connection with the above data, if we leave out of consideration the pure starch sample. The results are more or less discordant and in some cases quite unexplainable. For instance, the hay and cottonseed-meal when boiled with water, do not give the iodine reaction for starch, yet each of these special methods for the determination of starch credit them with from four to sixty per cent. of the same. Even fifteen minutes warming with very dilute hydrochloric acid gives an appreciable amount of what we are bound to interpret as starch. This brings us to the inevitable conclusion, that other bodies than starch are present and respond toward each of these reactions in the same way as starch does. We know moreover that the pentosans are such bodies and that they are invariably present to a greater or less degree in materials of the kind under examination.

In order to obtain some experimental data bearing upon the subject, portions of an isolated sample of pentosans were subjected to each of the methods under discussion. The material was, properly speaking, *xylan*, since on inversion it yields only xylose. It was obtained from wheat straw by boiling the same with lime-water and precipitating the xylan with alcohol. It possessed as high a grade of purity as has thus far been attainable in the preparation of these materials. It was free from any other form of carbohydrate and contained about six per cent. of ash materials.

One gram of xylan heated for thirty minutes with fifty cc. of water and four cc. of strong hydrochloric acid was entirely dissolved. The solution was neutralized and made up to 100 cc. Of this 6.7 cc. were required to reduce the copper from ten cc. of Fehling's solution, a result equivalent to 67.16 per cent. of starch.

One gram of xylan was heated with fifty cc. of ten per cent. nitric acid for one hour and became completely dissolved. The solution was made up to 100 cc. and polarized. The reading

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One gram of xylan was heated with fifty cc. of ten per cent. nitric acid for one hour and became completely dissolved. The solution was made up to 100 cc. and polarized. The reading

was equivalent to that produced by 44.73 per cent. of starch.

One gram of xylan was treated with fifty cc. of a concentrated solution of oxalic acid for one hour by which it became completely dissolved, made up to 100 cc. with ten per cent. nitric acid and heated another hour. The polariscope readings were the same as in the previous case, equivalent to 44.73 per cent. starch.

The salicylic acid method was not applicable.

One gram of xylan was boiled with thirty cc. of water, twenty-five cc. of barium hydroxide solution was added and afterwards thirty-five cc. of eighty-five per cent. alcohol and the whole made up to 100 cc. with water. Upon titration of the excess of barium hydroxide, an equivalent of 47.48 per cent. of starch was indicated.

These results show conclusively that the pentosan which is most characteristic of feeding stuffs and which has been shown to occur in all such materials, behaves, towards the reagents named, in precisely the same manner as starch and in a no less-marked degree. The conclusion is unavoidable that none of the methods for determining starch, based upon the above principles, can be employed with any degree of accuracy upon grains or forage plants or any materials where the presence of these pentosans is probable.

The most hopeful way of avoiding these difficulties would seem to be some method of bringing the starch into solution and removing it from its accompanying carbohydrates without any corresponding influence upon them. One method seems to offer this advantage; *viz.*, the application of diastase or malt infusion to the starch containing material. This method is recommended for use among the European Experiment Stations; it has been shown to yield accurate results with pure starch and can be objected to, if at all, only on account of length of time required and the difficulty of always having a proper preparation of diastase or malt infusion at hand. These are, however, minor objections in the light of greater accuracy secured. The general features of the method are as follows: The weighed material is boiled with water (most effectively under pressure) to convert the starch into a paste; after cooling to 65° C. a small quantity of malt

infusion is added and the temperature maintained at 60° to 65° for a half hour. The starch reaction having disappeared the solution may be filtered off washing the residue thoroughly, the filtrate warmed with a few cc. of acid to complete the conversion into dextrose and finally neutralized, made up to definite volume, and titrated. It remains to be seen what the effect of this process may be upon the pentosans or other similar bodies, concerning which there are few data at hand. I have made some preliminary tests which indicate that these bodies are not affected by diastase. One gram of the xylan, already mentioned, after boiling with water received ten cc. of a fairly strong infusion of malt and was kept at 65° C. for a half hour. At the same time a sample of starch was boiled to a paste, and treated with the malt infusion in the same way. The starch reaction disappeared and the solution reduced Fehling's solution strongly but the xylan did not change the Fehling's solution in the least nor did it appear to have been altered.

It seems, therefore, that in this last method the difficulties presented by the more common methods are to be avoided. The ordinary inversion methods on the other hand furnish no accurate conclusion when applied to the determination of starch contained in vegetable tissues.

For assistance in much of the analytical work cited I am indebted to Mr. D. B. Hoffmann.

NOTES ON THE HARDENING OF MORTAR.¹

BY WM. P. MASON.

THE following is extracted from the graduating thesis of Mr. J. A. McPherson, of the class of 1894, Rensselaer Polytechnic Institute, the work having been done in my department:

It is common belief among builders, that it is better practice to mix lime mortar and let it lie in a heap some days previous to use, rather than to employ it directly after preparation. In order to test this point, samples of mortar were taken, on successive days, from two separate heaps, of large size; briquettes were made therefrom, and, after an interval of some weeks, were broken for estimation of tensile strength with the following results:

¹ Read at the Brooklyn Meeting, August 16, 1894.

| | Days in heap
after
mixing. | Days exposed
to air as a
briquette. | Average breaking
weight in pounds
per square
inch. |
|-------------------|----------------------------------|---|---|
| Mortar No. 1..... | 3 | 50 | 34.6 |
| “ “ | 4 | 49 | 38.6 |
| “ “ | 6 | 48 | 38.1 |
| “ “ | 7 | 46 | 39.3 |
| Mortar No. 2..... | 4 | 48 | 36.0 |
| “ “ | 5 | 47 | 38.0 |
| “ “ | 6 | 46 | 41.2 |
| “ “ | 7 | 45 | 41.5 |

As concerning the formation of calcium silicate through the action of the lime upon the sand, the amount of such formation was found exceedingly small, even after great intervals of time.

After extended experiments with mortar taken from the old Van Rensselaer mansion at Albany, built about 1760, and with mortar from a very ancient tower in the valley of the Lahn, the quantity of calcium silicate found therein was 0.34 per cent. of the total weight of the mortar, an amount altogether too small to be considered as a factor in the hardening of the mortar.

The influence of tempering hydraulic mortar with water containing sugar (one-half pound of sugar to one gallon of water) is shown by the following averages, the mortar used having a tensile strength when tempered with pure water of sixty-three pounds per square inch.

Average tensile strength of sugared briquettes exposed to water during thirty-eight days was 62.75 pounds.

Similar briquettes exposed to air during same period was 65.4 pounds.

There is, therefore, a gain of three and eight-tenths per cent. over the water-tempered mortar in cases where the mortar is used in air, but no advantage when the mortar is intended for sub-aqueous work.

In South America there has been occasional use of bullocks' blood for tempering hydraulic mortar. In view of this, a number of experiments were made with the same mortar which was used in the sugar experiments, but the tempering was made

with bullocks' blood diluted with one-third its volume of water. The resulting briquettes set somewhat more quickly, and were very hard and firm. Their average tensile strength was:

After exposure to water during thirty-seven days, 68.3 pounds.

" " " air " " " " 69.8 "

Thus showing a gain over the water-tempering of ten per cent. for the briquettes set in air.

RENSSELAER POLYTECHNIC INSTITUTE,
June, 1894.

SOME ALLOYS OF IRON WITH MOLYBDENUM, TUNGSTEN AND CHROMIUM AS SOLUTIONS.

BY JAMES S. DE BENNEVILLE.

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THE results obtained by the action of silver nitrate on a ferro-tungsten of markedly heterogeneous character appeared to make a study of the reactions of the alloys of iron with the sixth family of interest. In the former paper¹ it was indicated, that a connection existed between the combining ratio of the two constituents and the chemical action of the compound toward reagents. The probable high valency of the iron atom in these metallic compounds, indicated by the fact that all that element appeared to be in combination with the tungsten; the chemical stability of the alloy and the very marked influence of the constituent tungsten on the compounds were noted, as also the nature of the alloy regarded as a solution. The work involved in the present paper is an attempt to broaden the scale of this previous investigation of one compound of a very interesting series. Alloys of the ferro compounds with the tungsten group were examined. The physical properties of these compounds as influencing their chemical properties were noted and the compounds analyzed and their quantitative composition established. The action of the weak solvent, silver nitrate, has been determined as also the reactions of the alloys with liquid and fused solvents. The discussion of the results obtained and their application to these alloys as solutions involved a short summary of the opinions expressed by others on valency and the nature of solution and the intimate connection between that state of matter and alloys.

¹ This JOURNAL, May, 1894.

The alloys were prepared by melting down cast iron with the metals at a white heat in a small Fletcher furnace working with a blast. One hour after reaching a white heat, the cast iron took up the quantity of the second metal indicated in the analyses. The melts were completely liquid and when cold were obtained in the form of buttons weighing twenty-five to thirty grams. The alloys investigated were ferro-molybdenum, ferro-tungsten and ferro-chromium.

FERRO-MOLYBDENUM.

Unalloyed molybdenum is practically infusible in furnaces working with blast. The metal probably could be obtained as a melt in the electric furnace as used by Moissan¹ in his investigations on the reduction by carbon of refractory oxides. As with many other metals of high melting-point, however, its alloys with the more fusible metals can be obtained at a much lower temperature. So with these iron compounds.

The information on these alloys is mainly due to Berthier and Thompson. Berthier states that molybdenum iron alloys are analogous to those with tungsten, a two per cent. molybdenum iron being fusible, very hard, brittle, but tenacious. Billings found that with one per cent. molybdenum, iron became red-short and worthless.² Thompson found that iron alloyed with molybdenum more readily than with any other metal. With equal parts of iron and molybdenum the alloy was fusible with the blowpipe. With thirty-three per cent. iron and sixty-seven per cent. molybdenum an alloy of a clear gray-white color was obtained. Twenty per cent. molybdenum iron was whiter than iron, very hard, brittle, tenacious, with granular fracture.³

The method of experiment followed was the use of the weak solvent silver nitrate to separate unstable alloys or the metals themselves from the more stable compounds. With the exception of chromium the elements under discussion all react with solution of the silver salt. Dr. Edgar F. Smith has shown⁴ that the reaction between metallic molybdenum and the silver

¹ Since this paper was written Mr. Moissan has reduced molybdenum in his electric furnace obtaining the metal as a melt, *i. e.*, fused mass. See *Bull. Soc. Chim.*, [3], 11, 857-5 Sept., 1894.

² Howe, *Metallurgy of Steel*, p. 86.

³ Hiorns, *Mixed Metals*, p. 359.

⁴ *Ztschr. anorg. Chem.*, 1, 360.

salt is very exact, silver being reduced to metal and molybdic acid formed. The ratio being Mo : 6Ag. With these iron alloys, the reaction is very complex owing to secondary reactions. The molybdenum is converted into the lower oxide of a blue color. On digesting with the neutral silver salt, no white precipitate of molybdic acid separates.

Separate portions of the alloys were crushed in a steel mortar and passed through a sixty mesh sieve. Weighed portions were then digested with excess of solution of silver nitrate. After twenty-four hours these solutions were decanted and the residue washed by decantation with water. The residue from treatment with neutral silver salt was digested with ammonia. This solution was filtered and added to the first and iron and molybdenum determined. The final residue was treated with nitric acid and, after removal of the silver, molybdenum and iron determined. By this method were obtained: 1. Iron replacing silver. 2. Molybdenum replacing silver. 3. Iron and molybdenum in stable combination.

The quantity of iron extracted by hydrochloric acid was determined. The alloys were not completely decomposed by the acid. A considerable portion of the iron was attacked but the molybdenum would be acted on only to a small extent and would appear in any ratio calculated between total iron and total molybdenum found in the residue. This did not afford a method of separating alloys soluble in the acid solvent.

The experimental results tabulated gave:

Alloy A. Nos. 1-4, close grained crystalline mass showing under the glass segregations marked by a slight yellowish tinge. This sample was fused to a clear button. Brittle, hardness 7, scratching quartz but not topaz. Fracture granular, of a silver-white color, gradually assuming, on exposure to air, a yellowish and in places a brownish tint. Strongly magnetic, not malleable, sp. gr. 8.182.

Alloy B. Nos. 5-12, appearance as with alloy A. strongly magnetic, somewhat malleable,¹ brittle, hardness seven, not so readily oxidized on exposure of fresh fracture to the atmosphere, sp. gr. 7.830

¹ Used relatively. Flattened slightly before crushing.

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These alloys slowly decompose water on boiling. The terms "free" iron and "free" molybdenum are used to indicate the iron and molybdenum replacing silver in the silver nitrate. "Free" is used in the same sense throughout the remaining experiments.

I. MOLYBDENUM ALLOYS WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

| No. | A. | B. | C. | D. | E. | F. | G | |
|-------|-----------|-----------|------------|------------|--------------|--------------|-----------|-----------|
| | Total Fe. | Total Mo. | "Free" Fe. | "Free" Mo. | Residual Fe. | Residual Mo. | A : B | E : F |
| 1 ... | 0.6710 | 0.3290 | 0.3638 | 0.0666 | 0.3072 | 0.2624 | 3.50 : 1 | 2 : 1 |
| 2 ... | 0.7106 | 0.2894 | 0.2608 | 0.1250 | 0.4498 | 0.1644 | 4.22 : 1 | 4.70 : 1 |
| 3 ... | 0.6694 | 0.3306 | 0.2162 | 0.0487 | 0.4532 | 0.2819 | 3.47 : 1 | 2.75 : 1 |
| 4 ... | 0.7084 | 0.2916 | 0.4932 | 0.1728 | 0.2152 | 0.1188 | 4.16 : 1 | 3.15 : 1 |
| 5 ... | 0.8703 | 0.1297 | 0.7185 | 0.0666 | 0.1529 | 0.0620 | 11.50 : 1 | 4.23 : 1 |
| 6 ... | 0.8893 | 0.1107 | 0.7154 | 0.0682 | 0.1529 | 0.0635 | 13.80 : 1 | 4.13 : 1 |
| 7 ... | 0.8584 | 0.1416 | 0.5706 | 0.0775 | 0.2879 | 0.0640 | 10.40 : 1 | 7.73 : 1 |
| 8 ... | 0.8104 | 0.1896 | 0.5328 | 0.1344 | 0.2776 | 0.0552 | 7.30 : 1 | 8.63 : 1 |
| 9 ... | 0.7882 | 0.2118 | 0.4634 | 0.1260 | 0.3248 | 0.0858 | 6.40 : 1 | 6.40 : 1 |
| 10... | 0.6670 | 0.3330 | 0.4939 | 0.1612 | 0.1731 | 0.1718 | 3.43 : 1 | 1.73 : 1 |
| 11... | 0.8414 | 0.1586 | 0.4832 | 0.0777 | 0.3582 | 0.0809 | 9.10 : 1 | 7.62 : 1 |
| 12... | 0.8883 | 0.1117 | 0.5406 | 0.0574 | 0.3478 | 0.0542 | 13.70 : 1 | 11.10 : 1 |

Taken for analysis 0.20-0.25 gram.

II. MOLYBDENUM ALLOYS WITH HYDROCHLORIC ACID, CALCULATED TO ONE GRAM.

| No. | A - 13. | B - 14. |
|------------------------------|---------|---------|
| Iron | 0.5982 | 0.6933 |
| Per cent. of total iron..... | 86.74 | 83.86 |

Taken for analysis, two grams.

III. MOLYBDENUM ALLOYS, CARBON, SILICON, PHOSPHORUS.

| No. | Sample. | Total Combined Graphitic | | | Si. | P. |
|---------|-----------------------|-----------------------------|-----------------------------|-----------------------------|------|------|
| | | C ₁
per cent. | C ₂
per cent. | C ₃
per cent. | | |
| 15..... | Pig iron ¹ | 2.99 | 0.37 | 2.62 | 2.92 | 0.33 |
| 16..... | Alloy A | 2.90 | 0.17 | 2.73 | 0.74 | 0.31 |
| 17..... | Alloy B | 2.97 | 0.20 | 2.77 | 0.66 | 0.30 |

A third sample was obtained by melting cast iron in the presence of twice its weight of molybdenum. At the heat obtained this was fused down to an irregular mass but a clean button was not obtained. It was very crystalline in structure, the luster in places being of the nature of "parrot" copper ore. The portion unattacked by the weak solvent is of interest, the remainder evidently containing unalloyed molybdenum. The "residual" iron and molybdenum obtained, gave :

¹ Sp. gr., 6.980.

IV. MOLYBDENUM ALLOYS, C.

| No. | Residual
Fe. | Residual
Mo. | Ratio. |
|---------|-----------------|-----------------|----------|
| 18..... | 0.7394 | 0.2606 | 4.85 : 1 |
| 19..... | 0.4267 | 0.5733 | 1.40 : 1 |
| 20..... | 0.1320 | 0.8680 | 1 : 5 |
| 21..... | 0.0770 | 0.9230 | 1 : 7 |

By HCl 42.63 per cent. of total iron dissolved.

In table I the analyses appear to show that the silver nitrate acts not only on unstable alloys but on iron as such or on molybdenum as such. The attacked and unattacked portion varies considerably through the mass. Table IV indicates the influence of mass action. The quantity taken for experiment (0.20–0.25 gram) was small and any marked differentiation would appear. If iron be regarded as limited in its lower compounds by divalency the formula Fe_2Mo (molybdenum being regarded as hexavalent) would represent the saturation-point corresponding to 63.64 per cent. iron and 36.36 per cent. molybdenum. If now the alloy contain less molybdenum than thirty-six per cent., either: 1. The iron in excess must be regarded as present as such in the same sense that water in excess is present in an unsaturated solution, or 2, the alloy is analogous to a cryohydrate, there being present a definite compound or compounds and the excess of the solvent, forming one homogeneous system in its liquid and melted condition, but in the solid (*i. e.* frozen) form making up a system in which the parts bear a definite relation to each other as in cryohydrates, or in which the excess of the solvent is present in a form analogous to ice in such mixtures. 3. That while there may be definite compounds formed in the alloy yet the main bulk of the system is in chemical union, all the iron being united to all the molybdenum no matter how large the quantity of either constituent. 4. That in solution the iron and the molybdenum may be in combination up to the full power of their respective valencies, but that this valency is not exercised (or its power decreases) on cooling, on which the more stable forms of combination appear. Iron or molybdenum in excess may then be present in the solidified alloy and it is not unlikely that owing to the very high melting-point of molybdenum that, as the fusing-point of the mixture rises, a part of the molybdenum exists as a mechan-

ical mixture either never having been in combination with the iron or separating out from the alloy on cooling and the exercise of the more stable valency.¹ The action of a weak solvent, as of any solvent, is mainly dependent on the affinity between the constituents of the compound. That iron and molybdenum form a stable alloy is evidenced by the fact that the action of strong hydrochloric acid fails to decompose these compounds but leaves a residue more or less rich in iron. The silver nitrate can then be regarded as a solvent of a definite compound or compounds in the solidified alloy acting on these and on the metal in excess but failing to attack the more stable compound. Both iron and molybdenum react with the silver salt and the failure of this reaction to take place with considerable percentage of the alloys also points to a strong affinity between the two elements. As with tungsten this is to be expected from the nature of molybdenum as semi-metal. Increased percentage of molybdenum accompanied increased brittleness and decrease in fusibility. The alloys were decomposed by nitric acid which converted the molybdenum to molybdic acid; by potassium bisulphate with evolution of sulphurous anhydride; by fusion with mixture of sodium carbonate and saltpeter; hydrochloric acid left a residue rich in molybdenum.

Analytical Methods.—The direct analysis of these molybdenum alloys (for iron and molybdenum) can be readily made by two methods. 1. The powdered alloy can be fused with oxidizing mixture with addition of caustic soda, cooled and lixivated in water and the soluble sodium molybdate separated by filtration from the residual ferric hydroxide. The molybdenum can then be determined by neutralizing with nitric acid the whole, or an aliquot portion of the solution of alkali molybdate, using methyl-orange as an indicator, and precipitating in the neutral solution as lead molybdate according to Chatard's method.² 2. A convenient method of analysis was found by solution in nitric acid. Excess of acid is removed by evaporation and excess of ammonia and ammonium sulphide is then added, digesting in a warm place for at least an hour and acidifying with hydrochloric acid and boil-

¹ Lothar Meyer, *Modern Theories of Chemistry*, pp. 307, 308.

² Fresenius, *Quantitative Analysis*, p. 353.

ing. Hydrogen sulphide is then passed through the hot solution until saturation. In the indirect analysis (with silver nitrate), after removing silver by hydrochloric acid, it was found necessary to oxidize the boiling solution by nitric acid otherwise the molybdenum remains partly in the form of the lower oxide which does not appear to be readily converted to sulphosalt and on dissolving the iron sulphide in hydrochloric acid the blue color indicates the molybdenum in solution. The precipitated molybdenum trisulphide is oxidized by nitric acid, filtered from any residual sulphur and the cold acid solution precipitated by barium nitrate avoiding an excess. The barium sulphate is filtered off, the filtrate neutralized by ammonia, leaving it barely but distinctly acid, and the molybdenum precipitated as lead molybdate. Throughout these analyses iron is determined volumetrically in sulphuric acid solution by titration with permanganate. A very pure zinc was used for reduction.

Table III explains itself. There appears a decided decrease in the percentage of silicon and a slight increase in the graphitic carbon over the combined. The phosphorus shows no change. The two analyses are only suggestive not indicative of these differences as due to the molybdenum. In determining both phosphorus and silicon the formation of phospho- and silicomolybdate,¹ at least partly soluble, must be taken into account. The graphitic carbon is that determined after treating the iron with hydrochloric acid. In ordinary steels the combined carbon is readily decomposed by the acid and the residue in these irons is probably free from combined carbon. Combustion of the powdered alloy only gave partial results. These alloys slowly decompose water on boiling. Their heterogeneity was apparent on so treating fragments of the alloys, brownish and yellowish spots due to oxidation being scattered over the exposed surface. These were distinct from the iron rust which was also formed. Metallic molybdenum decomposes water on boiling. The richer the alloy in molybdenum the more readily it decomposes water.

FERRO-TUNGSTEN.

The experiments in a former paper² on ferro-tungsten were

¹ See under ferro-tungsten.

² This JOURNAL, May, 1894.

made on an alloy containing, on averaging twelve analyses, 53 per cent. iron and 46.3 per cent. tungsten and of 10.14 sp. gr.¹ A second alloy of eighteen per cent. tungsten was made. The method of preparation and experimentation followed was the same as with the molybdenum compounds. The action of tungsten on silver nitrate has been found by Smith² to be analogous to that of molybdenum. Tungstic acid is formed and silver reduced to metal, the ratio being W : 6Ag.

In the alloy previously described (Nos. 22-26) it was found that the iron and tungsten were present in a very stable form, only a small percentage of tungsten and iron being attacked by the silver solution. In view of the more extended experiments this soluble portion can be regarded as a part of the alloy more readily attacked than the residue. Schneider separated from a high tungsten iron what appeared to be two alloys, one magnetic and the other non-magnetic corresponding to the formulas Fe_2W and Fe_3W . He used hydrochloric acid as a means of separation from the soluble iron.³ It must be taken into consideration, however, that tungsten is but little attacked by hydrochloric acid and in the case of an alloy of which the iron was readily attacked by acid it would be left in the residue and vitiate any ratio calculated from analysis of that residue. With silver nitrate, however, there is a definite reaction between the silver and the constituents of the alloy. They both act on it, although (and the varying ratios point to the latter alternative) the doubt exists as to whether the silver salt attacks a definite compound or varying quantities of alloys of different composition. The chemical inertness of these alloys is much more conspicuous than with the molybdenum compounds. Whatever compounds are formed in these alloys, are probably compounds made up of atomic linking and not the union of like molecules. These compounds are formed from a solution, and Heycock and Neville on determining the molecular weights of metals dissolved in sodium found for copper, silver, lead, antimony, zinc, cadmium and mercury, one atom in the molecule. Ramsay obtained like results by

¹ I am indebted to Dr. Wm. H. Wahl through Mr. F. Lynwood Garrison for this alloy.

² I am indebted to Dr. Smith in a private communication for reactions of molybdenum and tungsten bearing on these alloys. See *Ztschr. anorg. Chem.*, 1, 360.

³ Howe, *Metallurgy of Steel*, p. 81.

determination of the variation of vapor tension of mercury.¹

Analytical Methods.—The best method for direct analysis of these compounds was found to be fusion with the oxidizing mixture with addition of caustic soda and lixiviation in water. The soluble sodium tungstate was filtered from the residual ferric hydroxide and the tungsten precipitated in neutral solution by mercurous nitrate according to the method of Wolcott Gibbs.² In the indirect analysis, to the solution obtained on filtering from the unattacked residue, ammonia in excess was added and then ammonium sulphide. After digesting in a warm place for an hour this solution was acidified by hydrochloric acid and boiled. Hydrogen sulphide was then passed through it to saturation and the precipitate of silver sulphide and tungsten trisulphide filtered off and tungsten separated from silver by solution in ammonium sulphide. After removal of ammonium salts and oxidation, tungsten was determined as tungstic oxide, WO_3 . The unattacked residue, after removal of silver,³ was fused with oxidizing mixture and the sodium tungstate separated from the residual ferric hydroxide by lixiviation in water and filtration.

The experimental results gave:

Alloy D, Nos. 22–26.⁴ Crystalline with marked differentiation throughout the mass showing a number of cleavage planes of a pyritous appearance, also lining the cavities. The body or cementing portion of the alloy being finely crystalline but without the luster of the molybdenum compounds. Hard, brittle and tough. Sp. gr. 10.14. Alloy E, Nos. 26–29. Fine-grained crystalline mass without visible differentiation. Color, dark gray, the original pig iron being lighter in color. Brittle. Hardness barely 7. Sp. gr. 7.935. This alloy scratched glass readily; quartz only with difficulty. On boiling in water and subsequent oxidation this alloy showed patches of brown, yellow and bluish spots distinct from the iron “rust” formed.

¹ Mendelejeff, *Principles of Chemistry*, 1, 123. Ramsay obtained with barium, calcium, and potassium abnormal results, the number representing the first two metals being one-half the atomic weights. With potassium a number considerably less than its atomic weight was obtained.—*J. Chem. Soc. Trans.*, 1889, 521.

² Blair, *Chemical Analysis of Iron*, p. 123. Modified as described in Classen (trans. of Smith) p. 174.

³ This residue was not attacked by dilute nitric acid.

⁴ As described by Dr. Wahl.

These oxidation-points were distributed all through the mass with considerable uniformity.

V. TUNGSTEN ALLOYS WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

| No. | A.
Total
Fe. | B.
Total
W. | C.
"Free"
Fe. | D.
"Free"
W. | E.
Residual
Fe. | F.
Residual
W. | G.
Ratios
A : B. E : F. |
|------|--------------------|-------------------|---------------------|--------------------|-----------------------|----------------------|-------------------------------|
| 22.. | 0.5166 | 0.4834 | 0.0122 | 0.0403 | 0.5044 | 0.4431 | 3.51 : 1 3.74 : 1 |
| 23.. | 0.4109 | 0.5891 | 0.0283 | 0.0526 | 0.3826 | 0.5365 | 2.30 : 1 2.34 : 1 |
| 24.. | 0.5276 | 0.4724 | 0.0566 | 0.0370 | 0.4709 | 0.4355 | 3.66 : 1 3.54 : 1 |
| 25.. | 0.5270 | 0.4730 | 0.3156 | 0.0632 | 0.2093 | 0.5881 | 3.66 : 1 1.17 : 1 |
| 26.. | 0.5265 | 0.4735 | 0.0152 | 0.0541 | 0.5096 | 0.4211 | 3.66 : 1 4 : 1 |
| 27.. | 0.8053 | 0.1947 | 0.7104 | 0.0652 | 0.0949 | 0.1295 | 13.6 : 1 4.17 : 1 |
| 28.. | 0.8119 | 0.1881 | 0.7111 | 0.0760 | 0.1008 | 0.1121 | 14.1 : 1 3.4 : 1 |
| 29.. | 0.8124 | 0.1876 | 0.6980 | 0.0721 | 0.1144 | 0.1155 | 14.2 : 1 3.15 : 1 |
| 30.. | 0.8584 | 0.1416 | 0.7393 | 0.0331 | 0.1221 | 0.1055 | 20 : 1 2.6 : 1 |

Taken for analysis, 0.20-0.25 gram.

VI. TUNGSTEN ALLOYS WITH HYDROCHLORIC ACID, CALCULATED TO ONE GRAM.

| No. | D-31. | E-32. |
|------------------------------|--------|--------|
| Iron..... | 0.3728 | 0.6223 |
| Per cent. of total iron..... | 70.34 | 75.70 |

Taken for analysis, two grams.

VII. TUNGSTEN ALLOYS, CARBON, SILICON, PHOSPHORUS.

| No. | Sample. | Total
C,
per cent. | Combined
C,
per cent. | Graphitic
C,
per cent. | Si,
per cent. | P,
per cent. |
|---------|-----------------------|--------------------------|-----------------------------|------------------------------|------------------|-----------------|
| 33..... | Alloy D ¹ | 2.40 | 1.84 | 0.56 | 2.07 | 0.25 |
| 34..... | Pig iron ² | 3.06 | 0.77 | 2.29 | 3.30 | 0.32 |

These alloys also are marked by heterogeneity, containing more and less stable compounds. Their crystalline character is more prominent than with the molybdenum compounds, cavities in the alloys being lined with imperfect crystals by no means microscopic and showing cleavage planes of a pyritous appearance. Poleck and Grützner³ have examined one of these forms in a ferro-tungsten. Their description of the alloy is of a crystalline mass, dense and hard, of a steelish gray color, metallic luster, with cavities lined with small crystals, found by Hintze to be of the hexagonal system or possibly rhombohedral if hemihedral in form. They were nearly as hard as corundum and were completely attacked by sodium potassium carbonate, giving the formula FeW₃ analogous to FeS₃. The cementing material

¹ Made from tungsten and pig iron, No. 34.

² Sp. gr., 7.146.

³ Abstracted *Bull. Soc. Chim.*, No. 8, 1893.

gave the formula $\text{Fe}_3\text{W}_2\text{C}_3$, and was nearly as hard as the crystals. Density 12.92–13.14. F. N. Riddle¹ smelted Lake Superior hematite with tungstic oxide and carbon. In the crystalline mass were obtained steel-gray crystals insoluble in hydrochloric acid and found to contain 98–99.5 per cent. tungsten. Density 15–16. With nickel he states the separation of this crystalline tungsten was still more marked. The variation of results among different observers shows the influence the conditions of preparation have on alloys of iron and tungsten.

The chemical reactions of these tungsten alloys strongly indicated the influence of the tungsten. Acid solvents were practically useless as a means of analysis. Both nitric acid and aqua regia decompose them but very slowly and only by removing the protecting coating, the yellow hydroxide $\text{Wo}(\text{OH})_3$, and adding fresh acid. Potassium bisulphate (sulphuric acid at a red heat) decomposes them with evolution of sulphurous anhydride. An oxidizing mixture of sodium carbonate and saltpeter was a complete and ready means of decomposition, as also was caustic soda. Hydrochloric acid acts only partially on the iron. These reactions are those of metallic tungsten and indicate a combination of iron and tungsten equally inert.

The formation of phosphotungstate and silicotungstate, partly, at least, insoluble and remaining with the tungstic acid, necessitated some modification in the determination of these elements. The separation was made by fusing the powdered alloy with oxidizing mixture and caustic soda dissolving the melt and filtering from the residue. This residue was treated in the usual manner for silicon. To the solution containing alkali tungstate, silicate (in part), and phosphate, enough ferric chloride is added to precipitate silicic and phosphoric acid. The solution is now acidified, the ferric carbonate formed dissolving. Carbon dioxid is expelled by boiling, and ammonia in excess added to re-solution of precipitated tungstic acid. Silicic and phosphoric acids are now determined as usual. In determining arsenic and phosphorus in pig copper this method was found to be accurate, these elements going with iron in preference to lead, antimony, tin, or bismuth.²

¹ *Am. J. Sci.*, 1889, [3], 38, 160.

² Modification of a method described in Crookes' *Select Chemical Methods*, p. 430.

FERRO-CHROMIUM.

Since the publication in 1820 by Berthier¹ of his experiments on alloys of chromium with iron, these compounds have been carefully studied both from a chemical and physical standpoint with regard to their metallurgical application. Physically, chromium increases the hardness and tensile strength of iron, but makes it brittle. As noted in the discussion of ferro-molybdenum the properties of hardness and density appear to be connected with condensation, and in the case of both these properties they increase with the content of chromium. Brustlein² notes that the carbon increases with the chromium, giving a series from twelve per cent. chromium, two per cent. carbon to eighty per cent. chromium with eleven per cent. carbon. Howe³ also notes this increase of the carbon content and also that, as in the case of manganese, the chromium prevents the separation of graphitic carbon. According to the same authority chromium combines with iron "in all proportions or at least up to eighty per cent." the alloys being markedly heterogeneous in nature, samples from the same piece giving very different results when subjected to physical tests. He etched a plate of chrome steel with sulphuric acid and noted in it the presence of portions not attacked by the acid and which he considered probably to be alloys rich in chromium. The analyses made for this paper give the same results in regard to heterogeneity in these chromium alloys and in the other alloys examined and show the necessity of taking from half to one gram of an average for analysis. The experimental method pursued was the same as with the molybdenum and tungsten alloys. Nitric acid, dilute or concentrated, does not attack metallic chromium. The silver nitrate would not, therefore, attack the chromium constituent of these alloys. The action of the reagent, however, is of interest as showing the amount of iron in stable combination and the figures so obtained are given. The chromium alloys of iron show the influence of the chromium in almost as positive a manner as with tungsten compounds. Acid solvents act very slowly on high chrome alloys. Potassium bisulphate and the oxidizing mixture decompose them

¹ *Annales des Mines*, [1] 6, 573.

² Hiorns, *Mixed Metals*, p. 359.

³ Howe, *Metallurgy of Steel*, p. 75.

readily, and the latter energetically, the oxidation of the fine powder giving rise to a considerable evolution of heat which rapidly raises the crucible to bright redness; only one alloy was made.

Alloy F. Brilliantly crystalline; acicular, with a cleavage appearance like antimony. Brittle. Scratches glass with difficulty. Does not scratch quartz. Specific gravity, 7.464. Hydrochloric acid decomposed this alloy.

VIII. CHROMIUM ALLOY WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

| No. | A | B | C | D | E | A:B. |
|---------|-----------|-----------|------------|--------------|--------------------------|------|
| | Total Fe. | Total Cr. | "Free" Fe. | Residual Fe. | Residual per cent. total | |
| 35..... | 0.8706 | 0.0794 | 0.4832 | 0.3874 | 44.49 | 10:1 |
| 36..... | 0.8684 | 0.0804 | 0.4497 | 0.4187 | 48.21 | 10:1 |
| 37..... | 0.8481 | 0.0999 | 0.4770 | 0.3711 | 43.75 | 8:1 |
| 38..... | 0.9154 | 0.0360 | 0.5092 | 0.4062 | 44.37 | 24:1 |

Taken for analysis 0.20-0.25 gram.

IX. CHROMIUM ALLOY, CARBON, SILICON, PHOSPHORUS.

| No. | Sample | Total C, per cent. | Combined C, per cent. | Graphitic C, per cent. | Si, per cent. | P, per cent. |
|-----|---------------|--------------------|-----------------------|------------------------|---------------|--------------|
| | | | | | | |
| 40 | Alloy F..... | 2.46 | 1.64 | 0.82 | 3.37 | 0.29 |
| 41 | Pig iron | 3.06 | 0.77 | 2.29 | 3.30 | 0.32 |

No. 40 was made by melting No. 41 with ninety per cent. ferrochrome.

Analytical Method.—In direct analysis for determination of chromium and iron the fusion with oxidizing mixture was adopted and separation of the chromate from ferric hydroxide effected by filtration. In determining iron and chromium digested with silver salt, the insoluble residue was dissolved in aqua regia, the silver chloride filtered off and the solution made alkaline by sodium hydroxide, boiled and bromine added. The residue of ferric hydroxide was filtered from the chromate. In the acid filtrate the chromic acid was reduced by hydrogen sulphide and the boiling solution precipitated by ammonia. Adhering alkali, forming chromate on ignition, was tested for by mercurous nitrate.¹

GENERAL CONSIDERATIONS.

In connecting solutions and alloys the part that the metal in excess plays is that of water in aqueous solutions of salts. That

¹ A Method used for chromite analysis by Dr. F. A. Genth.

this is not a purely mechanical part but that a distinct force is acting between the components of a solution is evident from the modification both of solvent and of the dissolved substance. The physical state of the latter changes, probably assuming the liquid form,¹ and the specific gravity, refractive power, tension of vapor, boiling and freezing-points,² are affected often considerably. The thermic effect resulting in evolution or absorption of heat, and alteration in volume³ shown by contraction or expansion, further indicate chemical action. The combination is an indefinite one in so far as addition of the solvent is concerned; but the amount of dissolved substance is strictly limited by temperature and pressure (in the case of gases). Van 't Hoff has intimately connected gases and solutions comparing diffusion to evaporation and solution to vaporization. His experiments on osmotic pressure, showing that solutions obeyed the laws of gases and that Avogadro's law could be applied to them.

The formation of definite compounds in solution is well established, the halogen acids and nitric acid affording examples of solutions of constant boiling-point; and until that concentration is reached the products of evaporation are mainly water or, as the case may be, acid.⁴ The cryohydrates are also examples of this definite combination, and such substances as H_2SO_4 , H_2O and salts with water of crystallization. Although these very definite compounds are formed with water, solution itself is a homogeneous system⁵ and the existence of these compounds as such in the fluid cannot be asserted. Sterry Hunt, who considers solution as the type of chemical action in its "identification of the different," regards the state as one in which all definiteness is lost and in which we cannot assert the existence of any one compound, or even element, more than another.⁷ We can only possibly predict what, under altered conditions, we can obtain from it.⁸ He sums up the theory of solution as "the formation of

¹ Mendelejeff, *Principles of Chemistry*, 1, 70.

² *Ibid.*, 1, 86, 87.

³ Lothar Meyer, *Modern Theories of Chemistry*, 466, 481.

⁴ *Trans. Swedish Acad. Sciences*, Part 21, No. 17, 1886; quoted by Mendelejeff, 1, 64, 65. See translation by Ramsay, *Phil. Mag.*, 26, 81, 1888, from *Ztschr. phys. Chem.*

⁵ Ostwald, *Solutions*, p. 9, trans. by Muir.

⁶ *Ibid.*, p. 148.

⁷ *New Basis of Chemistry*, p. 22.

⁸ *Ibid.*, p. 10.

definite compounds with water accompanied with all the phenomena of chemical union," further addition of water giving rise either to decomposition and formation of new compounds or to admixture of "one definite solution or liquid species with another less dense solution, or with water." These compounds "being separable in a solid state by change of temperature or in a liquid state (theoretically) by gravity;" liquidity is but an accident of solution, depending on temperature and pressure.¹ Arrhenius from his investigations of the depression of the freezing-points and lowering of the vapor pressure of solutions of electrolytes came to the conclusion that the system was one of dissociation.² Mendelejeff bringing all such compounds as solutions, cryohydrates, colloids, and amorphous silicates, under the law of definite and multiple proportions regards solutions as fluid unstable definite chemical compounds in a state of dissociation.³

Alloys, with the exception of some of the amalgams, are solids at the ordinary temperature and require a more or less elevated degree of heat for fusion, their melting-point depending on that of their constituents and on the nature of the alloy. As solutions, therefore, they only exist at high temperatures and it is at those temperatures that the laws of solutions must be applied to them. As is the case with liquids, they may be saturated or unsaturated compounds, in the latter case one of the constituents being present in excess and acting as the solvent, *i. e.*, corresponding to the part excess of water plays in the solution of a salt. If the solution be regarded as a state of dissociation, then while the mass or the alloy is in the liquid state (fused) we have a homogeneous system, and two elements may be in unstable combination which on cooling, *i. e.*, solidifying or freezing, separate in definite compounds limited by the valency of the constituents, any excess of one of the elements being indicated by the presence of that element in an uncombined state. When, therefore, there is no excess indicated in an alloy of one constituent over another it can be justly assumed that all is in combination, and the presence of an excess of one of the metals

¹ Systematic Mineralogy, pp. 77, 78, 82.

² Ostwald, Solutions, pp. 189, 214. Trans. of Muir.

³ Mendelejeff, Principles of Chemistry, 1, 105.

would correspond to the ice present when an aqueous solution of a salt is cooled below its freezing-point, or to those compounds of salts with much water known as cryohydrates. The freezing-points of metals and their alloys, with a few exceptions, are much higher than the normal temperature, 15° C. In his study of the solution of liquids in liquids W. T. Alexeef found that two liquids mutually soluble, intermix in all proportions at certain temperatures. At lower temperatures the solubility is limited, finally reaching a minimum.¹ This may be and probably is the case with melted metals, but the condition in which we can observe and examine them corresponds, as said before, to the frozen state.² Hardness and indifference to chemical reagents have long been associated with condensation, increased density being generally associated with these properties and indicating complexity of structure advancing from the gaseous to the solid form.³ In liquids, although friction appears as a factor, yet there is free communication within the bounds of the liquid; a considerable condensation, however, takes place. In the conversion of steam, gaseous H_2O , to water and ice, Sterry Hunt found this condensation to be for water, 1192 H_2O , and for ice, 1094 H_2O ,⁴ and in mineral species increased density was found to be associated with hardness and chemical indifference.⁵ Ramsay in determining the molecular formulas of liquids by means of their molecular surface energy, found that condensation increased with fall in temperature and obtained for sulphuric acid of 1.82 sp. gr. the very complex formula not lower than $(H_2SO_4)_{11}$ at ordinary temperatures.⁶

Regarding alloys as solutions, many of their physical properties can be explained. The alloy changes its nature both physical and chemical, differing from its constituents in volume (*i. e.* density) and melting-point, and forming often definite molecular compounds. This modification of its properties is greater or

¹ Mendelejeff, *Principles of Chemistry*, 1, 74. and Ostwald, *Solutions*, p. 40, trans. of Muir.

² *Ibid.*, 1, 105.

³ Sterry Hunt, *Systematic Mineralogy*, p. 86, seq.

⁴ *New Basis of Chemistry*, p. 109.

⁵ Researches of J. B. Mackintosh, *J. Anal. Chem.*, 1, 10. Sterry Hunt, *Systematic Mineralogy*, p. 93.

⁶ *J. Chem. Soc.*, 63, 1089, Sept. 1893. 65, 167, March, 1894.

less according as the constituents are separated in their nature. Mendelejeff cites the series formed by sodium with chlorine, sulphur, phosphorus, arsenic, antimony, tin, and zinc, changing its properties from the distinctly saline sodium chloride to the sodium zincide and with this change in properties as the union is with the element more and more like in nature to sodium increasing in valency; but they are distinct and definite compounds and not to be distinguished on the ground of chemical nature. He notes the same properties in the union of metallic oxides, instancing the large number of complex aluminum silicates in which the two constituents are very like in nature acting as feeble base or feeble acid, and united in such a substance as lava glass in varied proportions giving on crystallization definite compounds, the 'silicates.' The analogy between these vitreous substances, with their microcrystalline structure, and alloys is a striking one.

The question of variable valency of the elements arises in these compounds of like elements. Are they to be regarded in the same light as with those of rigidly defined proportions with unlike elements? This is evidently the case. Definite crystallized compounds of alloys are known, with well-defined properties unlike those of either of the constituents. The alloys SnCu , and SnCu_2 , as also PbSn , are examples. Polymerism has also its analogue in allotropism.² But in the union between unlike elements this variability appears. Sodium forms several oxides, as likewise gold, silver, copper, etc. The elements under consideration, chromium, molybdenum, and tungsten, unite with oxygen in several ratios. These latter are especially interesting in their relation to the silicates. The complexity of their silico-compounds and phospho-compounds, was long ago established by Wolcott Gibbs³ and if this complexity is related to the union of like properties in these oxides the same complexity is to be expected in the union of elements of like nature—as these metals. These alloys in the melted state are solutions, as the melted lava glass is a solution. There is a homogeneous system

¹ Mendelejeff, *Principles of Chemistry*, 1, 111, 112. See Matthiessen's *Conclusions*, *Brit. Ass. Reports*, 1863, p. 97, cited in Fownes' *Chemistry*, p. 290.

² Ernest Meyer, *History of Chemistry*, pp. 377, 454.

³ Gibbs, *Am. J. Sci.*, [3], 14, 61.

the equilibrium of which is disturbed on cooling and at different temperatures different salts crystallize out. These salts may represent combinations of the atoms as truly as NaCl or they may be molecular compounds of a salt with the solvent metal, *i. e.*, present in definite proportion analogous to water of crystallization as in the salt $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The number of such compounds separating out during the slow cooling of an alloy may be, and probably is, very great. In many alloys with slow cooling, a macrocrystalline structure often results, but with rapid cooling the result is the microcrystalline form. This is of such importance that the commercial use of many alloys requires their rapid cooling, from their tendency to coarsely crystalline structure and consequent loss of homogeneity. That the valency of an element is related to its electro-chemical behavior has been shown and the value of an element increases toward like elements and decreases or concentrates itself in union with unlike elements, *i. e.* "Elements of variable valency exercise the smaller valency when combining with those for which they have the greater affinity but the higher valency when uniting with those for which they have but small affinity." The possibility of self-saturation must be taken into account¹ and valency established on indirect determination is doubtful. In these compounds or alloys the question of valency becomes a very difficult one. The quantitative composition of a well-developed individual, such as a crystal, is no guide in itself to the valency of the constituents as crystallization is essentially molecular. We know that the passage from gas to liquid and to solid involves a condensation and most frequently a very great condensation of volume, and experiment on the solutions of metals in mercury and in sodium show many of them to be monatomic; therefore, while the molecule itself may contain but a comparatively small number of atoms, the union of these simple molecules to form larger ones brings about great complexity of structure indicated by the increased density, hardness, and chemical inertia. If this is the case the molecule of these ferro-compounds must be very complex and assuming the simplest formulas from the

¹ Lothar Meyer, *Modern Theories of Chemistry*, p. 349.

² *Ibid* on valency, p. 307 seq.

analyses—which, while representing the average of a number of alloys in the solid state, can be carried back to the liquid state when the system was homogeneous—very large integral weights or equivalents are obtained. The valency of iron to tungsten is at least equal to its valency to chlorine or to oxygen, and these are only minima. Ruthenium and osmium have been shown to be at least octovalent, and if the ammonia (NH_3) in the ammonium cobalt salts be considered as atomic and not molecular, cobalt, a metal closely allied to iron, must be accepted as dodecavalent.¹ The ratios obtained in column G of the tables do not afford an indication of the value of the iron atom in these alloys. The ratio E:F of the residues give for the highest formulas Fe_{11}Mo and Fe_7W , but unquestionably represent mixtures.² The presence of an allotropic form of iron, β iron, as taught by Prof. Osmond, is also to be taken into account. These elements of the sixth family, tungsten and chromium, come under the list of β forming elements. As far as the solution of steels in acids or in the copper alkali salt, this β or hard “adamantine” form of iron appears to act as other modifications. There is no reason to believe it would act differently with silver nitrate.³ The influence of mass appears in the increased ratio of the predominant metal in E:F. This is not so marked in the case of tungsten. A considerable uniformity runs through the analyses but several numbers (as I, 8, 9, 10) evidently mark points of segregation.⁴

¹ Lothar Meyer, *Modern Theories of Chemistry*, pp. 347, 348.

² The silicides and phosphides of iron are very inert. A ferro-silicon containing fifteen per cent. silicon was insoluble in nitric or hydrochloric acid, but soluble in aqua regia.

³ Prof. Osmond in his paper (*J. Iron and Steel Inst.*, p. 38, 1890) ascribes the power of retaining at the normal temperature iron in this β or hard form, to a number of elements among them tungsten and chromium; the hardness of such iron being due not only to the mechanical strains set up in the solid on cooling but to molecular strains, perhaps due to osmotic pressure exerted by elements of small atomic volume (discussion of Prof. J. O. Arnold's paper, May, 1893). Prof. Arnold considers the hardening property as due to mechanical strains on cooling probably caused by the formation of definite compounds such as Fe_3C . These authorities do not appear to regard as worthy of notice the theory that all the carbon, phosphorus, silicon, etc., is uniformly distributed through the iron and in combination with it; and in view of the small quantities of such elements present such a view appears chemically untenable. I am indebted to Mr. Garrison, who kindly brought these papers to my attention and placed them at my disposal for consultation.

⁴ In the action of silver nitrate on these alloys there is a considerable evolution of heat. This is also the case with iron.

the equilibrium of which is disturbed on cooling and at different temperatures different salts crystallize out. These salts may represent combinations of the atoms as truly as NaCl or they may be molecular compounds of a salt with the solvent metal, *i. e.*, present in definite proportion analogous to water of crystallization as in the salt $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The number of such compounds separating out during the slow cooling of an alloy may be, and probably is, very great. In many alloys with slow cooling, a macrocrystalline structure often results, but with rapid cooling the result is the microcrystalline form. This is of such importance that the commercial use of many alloys requires their rapid cooling, from their tendency to coarsely crystalline structure and consequent loss of homogeneity. That the valency of an element is related to its electro-chemical behavior has been shown and the value of an element increases toward like elements and decreases or concentrates itself in union with unlike elements, *i. e.* "Elements of variable valency exercise the smaller valency when combining with those for which they have the greater affinity but the higher valency when uniting with those for which they have but small affinity." The possibility of self-saturation must be taken into account¹ and valency established on indirect determination is doubtful. In these compounds or alloys the question of valency becomes a very difficult one. The quantitative composition of a well-developed individual, such as a crystal, is no guide in itself to the valency of the constituents as crystallization is essentially molecular. We know that the passage from gas to liquid and to solid involves a condensation and most frequently a very great condensation of volume, and experiment on the solutions of metals in mercury and in sodium show many of them to be monatomic; therefore, while the molecule itself may contain but a comparatively small number of atoms, the union of these simple molecules to form larger ones brings about great complexity of structure indicated by the increased density, hardness, and chemical inertia. If this is the case the molecule of these ferro-compounds must be very complex and assuming the simplest formulas from the

¹ Lothar Meyer, *Modern Theories of Chemistry*, p. 349.

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analyses—which, while representing the average of a number of alloys in the solid state, can be carried back to the liquid state when the system was homogeneous—very large integral weights or equivalents are obtained. The valency of iron to tungsten is at least equal to its valency to chlorine or to oxygen, and these are only minima. Ruthenium and osmium have been shown to be at least octovalent, and if the ammonia (NH_3) in the ammonium cobalt salts be considered as atomic and not molecular, cobalt, a metal closely allied to iron, must be accepted as dodecavalent.¹ The ratios obtained in column G of the tables do not afford an indication of the value of the iron atom in these alloys. The ratio E : F of the residues give for the highest formulas Fe_{11}Mo and Fe_4W , but unquestionably represent mixtures.² The presence of an allotropic form of iron, β iron, as taught by Prof. Osmond, is also to be taken into account. These elements of the sixth family, tungsten and chromium, come under the list of β forming elements. As far as the solution of steels in acids or in the copper alkali salt, this β or hard “adamantine” form of iron appears to act as other modifications. There is no reason to believe it would act differently with silver nitrate.³ The influence of mass appears in the increased ratio of the predominant metal in E : F. This is not so marked in the case of tungsten. A considerable uniformity runs through the analyses but several numbers (as I, 8, 9, 10) evidently mark points of segregation.⁴

¹ Lothar Meyer, *Modern Theories of Chemistry*, pp. 347, 348.

² The silicides and phosphides of iron are very inert. A ferro-silicon containing fifteen per cent. silicon was insoluble in nitric or hydrochloric acid, but soluble in aqua regia.

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⁴ In the action of silver nitrate on these alloys there is a considerable evolution of heat. This is also the case with iron.

That the melting-point of alloys is not the mean of the melting-points of their constituents but is influenced by properties probably chemical, is well known. An example of this is afforded by platinum which is only fusible by the oxyhydrogen flame in a lime furnace, but which with iron forms a readily fusible alloy at the highest temperature of the blast-furnace and also with a number of other elements, alloys fusible at the heat of the Bunsen lamp. This lowering of temperature is found with other still more infusible elements of this group; *viz.*, palladium, iridium, ruthenium, and osmium.¹ Tungsten, molybdenum, and chromium, form a group of very infusible substances but these iron alloys are formed readily at the temperature of the blast-furnace. Hardness, chemical indifference, and density are associated with molecular complexity and the tungsten group in their metallic forms are probably represented by formulas expressing great condensation and affinity between the like atoms. The formation of these iron alloys, therefore, must be preceded by a breaking up of this union between like atoms and molecules and this is brought about by a state of solution. The affinity of iron and the sixth family is then greater than the affinity of the like atoms, for on cooling from the homogeneous system of solution stable alloys of iron and the second constituent separate out. Now, as before cited, Heycock and Neville found (confirmed by Ramsay) that on determining the molecular weights of the metals dissolved in sodium and in mercury the results gave one atom in the molecule for a large number of metals, indicating that in solution in metals, a state of dissociation exists analogous to that of the aqueous solution. If this holds good, therefore, for these iron compounds, that in the liquid or melted condition the complex molecule of iron and tungsten existing in the solid state is broken up into a simpler form, then the affinity between the constituents of these alloys can act. The investigators found that on dissolving the metals in atomic proportions in molten tin on applying Raoult's method² to the lowering of temperature of solidification a constant was obtained, this being in accordance with Coppet's law

¹ Howe, *Metallurgy of Steel*, p. 79. A. Joly., *Compt. rend.*, 1893, 116, 430, on melting-point of the platinum metals.

² See *Am. Chem. J.*, 11, 67, 72.

that "solutions whose contents are in the ratio of the molecular weights of the dissolved salts freeze at nearly the same temperature." That is, the freezing-point is a function of the molecular weight. Indium and aluminum gave abnormal results indicating a more complex molecule in solution.

Chemical action is also indicated by change in volume and in his researches on dilute solutions Ostwald determined the amount of chemical change—in this case representing the avidity of the acids—by the contraction or expansion of the liquid.¹ With alloys, the same phenomena is observed. As a rule with the formation of definite compounds, *i. e.*, on cooling, contraction ensues. Alloys of bismuth, however, expand being analogous in this respect to ice. These iron alloys show change in volume, indicating by their increased density that with them a contraction has taken place. In every case there is a marked increase in specific gravity. Comparing the specific gravities:

X. TABLE ON COMPARATIVE DENSITIES.

| Nos. | Samples. | Sp. gr. of metal. | Sp. gr. of alloy. | Composition. | Sp. gr. of pig iron. | From composition, difference. | Equivalent weights. |
|-------|----------|-------------------|-------------------|----------------------------------|----------------------|-------------------------------|---------------------|
| 1-4 | A..... | Mo=8.6 | 8.182 | Fe ₄ Mo | 6.980 | +0.88 | 175052 |
| 5-12 | B..... | | 7.830 | Fe ₈ Mo | 6.980 | +0.67 | 167562 |
| 22-26 | D..... | W=19.2 | 10.140 | Fe ₇ W ₂ | | | 216996 |
| 27-30 | E..... | | 7.935 | Fe ₁₆ W | 7.146 | +0.08 | 169809 |
| 35-38 | F..... | Cr=6.8 | 7.446 | Fe ₂₀ Cr ₃ | 7.146 | +0.27 | 159629 |

Fe here represents the complex compound containing phosphorus, silicon, and carbon—pig iron. The sign—minus is to be expected with chromium. If these alloys are to be considered as chemical compounds and as atoms bound together into molecules and these molecules into still more complex molecules then these composition formulas, can be taken as representing the simplest average composition of the definite compounds in the alloy in the solid state. There may be and certainly are compounds in these alloys represented by formulas more complex than these simple formulas, for the elements, carbon, silicon, etc., have not been taken into account. Assuming these latter, however, column VI gives the equivalent weights $H_2O = 21400$.

¹ *J. Chem. Soc. Trans.*, 1889, 666, 1890, 376. Ramsay, *Ibid*, 1889, 521. Quoted in Ostwald, *Solutions*, p. 231, by Muir.

² Lothar Meyer, *Modern Theories of Chemistry*, p. 481 seq.

These high equivalents explain the physical properties, such as hardness and density, and the chemical inertia of these compounds.¹

In this connection it should be noted that there is a difference in density in a metal as solid and when in the melted condition. Wrightson² in his experiments on the relative specific gravity of cast iron in the two states found that the maximum volume was obtained on passing from the liquid to the solid. The same result was obtained from experiments made on melting solid iron or on cooling molten iron to solid. In the latter case there was observed: first an expansion, followed by contraction and again by expansion. The observed differences were small. Henri Moissan in his experiments on carbon dissolved in iron made use of this change of volume of the iron to subject the carbon, on sudden cooling, to great pressure.³

From these results it can be concluded:

1. That these alloys by their resistance to chemical reagents, their hardness and increased specific gravity, indicate a chemical union between the constituents. That in these alloys there are present a number of compounds, some of which are more stable than others, the latter being readily attacked by weak solvents. That these compounds are distributed with considerable uniformity throughout the mass of the alloy, segregation being the exception, not the rule, and that their freezing-points must be approximately the same, preventing the segregation of alloys of great density in any one portion of the alloys; that the more stable of these alloys are definite chemical compounds; that the less stable may be definite compounds or of the nature of cryohydrates or with one of the constituents present in the mixture in a state analogous to that of ice in a frozen salt solution in which water is in excess.

2. That, therefore, in these alloys the existence of definite compounds differing in their action toward solvents; their contraction as indicated by their specific gravity, hardness, etc., the fact that chemical union exists involving the breaking up of the

¹ Sterry Hunt, *New Basis of Chemistry*, p. 51 seq. and 100. *Systematic Mineralogy*, p. 86.

² Howe, *Metallurgy of Steel*, p. 254.

³ *Bull. Soc. Chim.*, 11, 8, January, 1893.

complex iron, molybdenum, tungsten, and chromium molecules and their union to form a new compound, *i. e.*, the passing of a heterogeneous system of molecules of like elements to a homogeneous system in the melted condition and again to a heterogeneous system in the resultant alloy; that these properties indicate a condition in these alloys analogous to an aqueous solution of a salt converted by cold to the solid state.

3. The high melting-point of the element in combination with the iron and its chemical affinity for iron is especially favorable to the separation of alloys from the cooling solution, and is the cause of the heterogeneity of these compounds. This separation of salts, *i. e.*, segregation, draws the analogy between these alloys and solutions closely.

XI. COMPOSITION OF ALLOYS.

| Alloys. | A. | B. | C. | D. | E. |
|---------------------|--------|--------|------------|--------|--------|
| Molybdenum | 0.2979 | 0.1665 | | | |
| Tungsten | | | 0.4646 | 0.1696 | |
| Chromium | | | | | 0.0702 |
| Iron | 0.6626 | 0.7942 | 0.5251 | 0.7832 | 0.8799 |
| Phosphorus | 0.0031 | 0.0030 | 0.0004 | 0.0025 | 0.0029 |
| Silicon | 0.0074 | 0.0066 | 0.0014 | 0.0207 | 0.0337 |
| Combined carbon... | 0.0017 | 0.0020 | } 0.0075 { | 0.0184 | 0.0041 |
| Graphitic carbon... | 0.0273 | 0.0277 | | 0.0056 | 0.0082 |

THE PROTEIDS OF THE KIDNEY BEAN.

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

(Continued from page 712.)

Another trial was made by treating 400 grams of bean-meal, previously exhausted by benzine, with one per cent. sodium chloride solution, dialyzing the extract for twenty-four hours, and filtering off the precipitated phaseolin. The clear filtrate after standing over night, deposited a considerable quantity of proteid, but the solution with this deposit was returned to the dialyzer and left for two days longer, when it was filtered, the precipitate washed with water, alcohol, and ether, dried over sulphuric acid, and six grams of preparation 36 obtained.

PHASELIN, PREPARATION 36.

| | | Ash-free. |
|----------------|-------|-----------|
| Carbon | 50.44 | 51.41 |
| Hydrogen | 7.14 | 7.28 |
| Nitrogen | 14.31 | 14.59 |
| Sulphur | 0.46 | 0.47 |
| Oxygen..... | | 26.25 |
| Ash | 1.94 | |
| | | 100.00 |

The filtrate from preparation 36 was then dialyzed into distilled water which was renewed every twenty-four hours for several days. After a week the solution was filtered and the precipitate washed with water, alcohol, and ether, and dried over sulphuric acid. It weighed 1.60 grams, 37.

PHASELIN, PREPARATION 37.

| | I. | II. | Average. | Ash-free. |
|-----------------|-------|-------|----------|-----------|
| Carbon..... | 51.38 | 51.22 | 51.30 | 52.19 |
| Hydrogen | 7.25 | 6.99 | 7.12 | 7.24 |
| Nitrogen | 14.52 | | 14.52 | 14.79 |
| Sulphur } | | | | 25.78 |
| Oxygen } | | | | |
| Ash | 1.83 | 1.61 | 1.72 | |
| | | | | 100.00 |

One more preparation, 38, was made in the same manner as 37, and had the following composition:

PHASELIN, PREPARATION 38.

| | | Ash-free. |
|----------------|-------|-----------|
| Carbon | 50.20 | 51.27 |
| Hydrogen | 7.07 | 7.22 |
| Nitrogen | 14.02 | 14.32 |
| Sulphur | 0.50 | 0.51 |
| Oxygen..... | | 26.68 |
| Ash | 2.06 | |
| | | 100.00 |

Further dialysis in distilled water, of the filtrate from preparation 37, gave no more precipitate. The solution was therefore saturated with ammonium sulphate, and the precipitate so produced filtered off and dissolved in distilled water. This solution which now had a volume of about 400 cc. was dialyzed for some

days, first in river water, and afterwards in distilled water, but only a trace of substance separated. This was filtered off, and the perfectly clear solution gave the following reactions:

Saturation with sodium chloride produced no precipitate until acetic acid was added. Acetic acid in the absence of salt gave no precipitate. Nitric acid gave a turbidity when added in considerable quantity, and the addition of some sodium chloride produced no further precipitation. Copper sulphate gave no precipitate. This solution when heated became turbid at 57° and particulate at 63° .

The entire solution was therefore heated to 70° in a water-bath which did not exceed this temperature, and after two hours, filtered from the separated coagulum. This was then washed with distilled water, alcohol, absolute alcohol, and ether, and dried over sulphuric acid. It weighed 0.48 gram. Before drying, this coagulum dissolved readily in two-tenths per cent. hydrochloric acid, and in dilute potash solution, and gave a violet reaction with copper sulphate and caustic potash. The filtrate from this coagulum gave a further small coagulum when heated at 70° , for some time longer. This was filtered off, and after treating it in the same way as the first coagulum, was added to it. The total amount of coagulum, preparation 39, amounted to 0.63 gram, and after drying at 110° was found to contain, ash-free, 15.23 per cent. of nitrogen.

The filtrate from 39 was then dialyzed into alcohol, and the solution thereby concentrated. On adding an equal volume of strong alcohol, the proteid was precipitated. This was filtered off, washed with absolute alcohol and ether, and dried over sulphuric acid. It then weighed 0.72 gram which shows that the proteids had been almost wholly precipitated by dialysis and coagulation.

This substance gave a nearly clear solution with distilled water, not made clearer by adding a few drops of sodium chloride solution. With caustic potash and copper sulphate, a pink color was developed which had a distinct violet tinge, and was by no means so red as that given by pure proteoses and peptones.

The aqueous solution heated to 85° gave a flocculent coagulum which apparently represented most of the substance. From

this, it would appear that true proteoses are present in extremely small amounts.

Dried at 110°, this preparation, 40, contained, ash-free, 13.60 per cent. of nitrogen. Being thrown down by strong alcohol, it could scarcely be pure, and the nitrogen determination is only of value, as indicating that the coagulum mainly consisted of proteid.

Of these preparations, 25, 27, and 32, are unquestionably mixtures of phaseolin and phaselin. Excluding these three and also 38 and 40, evidently impure, the remaining agree fairly well, as is shown by the following table:

SUMMARY OF ANALYSES OF PHASELIN FROM THE KIDNEY BEAN.

| | 26. | 28. | 29. | 30. | 31. | 33. |
|----------------|-------|--------|-------|--------|--------|-------|
| Carbon..... | | 51.57 | | 51.59 | 51.98 | |
| Hydrogen..... | | 6.92 | | 6.71 | 6.82 | |
| Nitrogen..... | 14.57 | 14.48 | 14.81 | 14.84 | 14.53 | 14.85 |
| Sulphur } | | 27.03 | | 26.87 | 26.68 | |
| Oxygen } | | | | | | |
| | | 100.00 | | 100.00 | 100.00 | |

| | 34. | 35. | 36. | 37. | 38. | Average. |
|----------------|--------|--------|-----------|--------|-----------|----------|
| Carbon | 51.38 | 51.37 | 51.41 | 52.19 | 51.27 | 51.60 |
| Hydrogen | 6.91 | 7.10 | 7.28 | 7.24 | 7.22 | 7.02 |
| Nitrogen | 14.67 | 14.71 | 14.59 | 14.79 | 14.32 | 14.65 |
| Sulphur } | 27.04 | 26.82 | { 0.47 } | 25.78 | { 0.51 } | 0.49 |
| Oxygen } | | | { 26.25 } | | { 26.68 } | 26.24 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

It is probable that these analyses pretty closely represent the true composition of this proteid, the various preparations having been made under such diverse conditions as to exclude the possibility of their being mixtures of the phaselin with non-proteid substances.

Preparations 26 and 28 were precipitated by heat, 29 and 30 by acid. Preparations 31, 34 and 35 were thrown down by alcohol, extracted by water from the precipitate so produced, and separated from the solution—31 by acid, and 34 and 35 by dialysis in alcohol. Finally, 36, 37, and 38 were obtained by fractional dialysis in water.

There is some difficulty in deciding to what class of proteids phaselin should be assigned. It most nearly agrees with the

globulins, being precipitated by dialysis after nearly all the salts are removed, and thereby largely converted into an insoluble form. Complete precipitation is not accomplished, even by prolonged dialysis in distilled water, and it may be questioned whether the precipitation that occurs on dialysis in water, is not the result of transformation into "albuminate."

Nitric acid in sufficient quantity gives a precipitate which, on warming, does not dissolve in the manner characterizing proteoses. Saturation with sodium chloride, gives only a slight precipitate, but further addition of acetic acid, occasions an abundant precipitate. With copper sulphate and caustic potash a violet color is produced.

The coagulum produced by heat, dissolves in one-tenth per cent. hydrochloric acid when heated to 80°. The temperature at which coagulation commences, varies with the amount of salts present, a turbidity usually appearing between 40° and 50° in solutions which have been dialyzed until the greater part of the phaseolin had been separated. The ten per cent. sodium chloride extract of the bean-meal, became turbid at 52°-55°, flocks forming at 68°-70°. The aqueous extract of the meal, heated to 60° gave a turbidity but slightly increased by boiling. When ten per cent. of sodium chloride was added to the aqueous extract, turbidity occurred at 37° and flocks formed at 52°. The coagulation of this proteid by heat, proceeds very slowly and is completed only by very prolonged heating, for days even, at a temperature considerably higher than that at which flocks first appear.

Amount of Proteids in the Kidney Bean.

The quantities of these two proteids occurring in the kidney bean cannot be accurately determined, owing to the difficulties encountered in separating them. An approximate estimate is as follows:

1. A sample of freshly ground air-dry bean-meal yielded by combustion, 3.785 per cent. of nitrogen. Considering all the nitrogen to exist as proteids containing sixteen per cent. of this element, the proportion of proteids in the bean-meal would be $(3.785 \times 6.25 =) 23.65$ per cent.

2. Twenty grams of bean-meal were treated repeatedly with

ten per cent. sodium chloride solution, until no more proteids could be extracted. The residue, after washing with water, alcohol, and ether, weighed, air-dry, 11.41 grams and contained 1.877 per cent. or 0.214 gram of nitrogen, equivalent to 1.338 grams of salt-insoluble proteid, which amounts to 6.69 per cent. of the meal. The salt-soluble proteids were accordingly $(23.65 - 6.69 = 16.96)$ seventeen per cent. of the meal.

3. In making preparations 4, 5, 6, and 7, pp. 638-9, the phaseolin obtained from the salt extract amounted to 14.77 per cent. This when weighed was not altogether pure or dry, but on the other hand, a part of this proteid existing in the salt extract, was not recovered, so that it may be fairly assumed that the meal contains about fifteen per cent. of salt-soluble phaseolin. This deducted from the seventeen per cent. of total salt-soluble proteids, leaves two per cent. for phaselin, reckoned water-free, other proteids being present in very minute quantity.

4. The preparations 36, 37, 39, and 40, pp. 758-60, were obtained from one and the same portion, 400 grams, of bean-meal, after phaseolin had been as completely removed as practicable. These preparations after drying over sulphuric acid, weighed respectively 6.00, 1.60, 0.63, and 0.72 grams, their total weight being 8.95 grams, equal to 2.24 per cent. of the meal. Their average nitrogen content was 14.54 per cent., very nearly that of phaselin. Making liberal allowance for impurities and incomplete drying, they represent about two per cent. of phaselin.

5. Twenty grams of bean-meal were extracted as completely as possible with two-tenths per cent. potash water. The washed and air-dry residue weighed 11.27 grams, and contained 0.91 per cent. or 0.1026 gram of nitrogen, equal to 0.611 gram of (water-free) proteid insoluble in alkali, or to 3.06 per cent. of the meal. The alkali-soluble proteid amounted therefore to $(23.65 - 3.06 = 20.59)$ 20.6 per cent. of the meal.

6. On page 642 is recorded that the proteid insoluble in salt solution, but dissolved by two-tenths per cent. potash, 15, contained sixteen per cent. of nitrogen and accordingly had nearly the composition of phaseolin. It is, therefore, probable that the proteid undissolved by salt-solution, is phaseolin. On this assumption, the kidney bean examined, contains about 21.5

per cent. of phaseolin, and about two per cent. of phaselin.

7. The foregoing data are summarized as follows: The "white medium field bean" contains approximately:

| | | |
|---|------|-----------|
| Phaselin, salt-soluble..... | 2 | per cent. |
| Phaseolin, salt-soluble | 15 | " |
| Phaseolin, salt-insoluble, alkali-soluble | 3.5 | " |
| Phaseolin, insoluble in salt and in 1% per cent. alkali | 3 | " |
| Total proteids | 23.5 | " |

Schulze, Steiger and Maxwell have stated¹ that ten per cent. of the nitrogen of the seeds of the horse bean (*Vicia faba*) the vetch and the pea, exists in non-proteid form. Should such prove to be the case with the kidney bean, then its total proteids would be about twenty-one per cent. instead of 23.5 per cent.

CONCLUSION.

The kidney bean contains two globulins characterized by great solubility in very dilute saline solutions, and by yielding precipitates with acids which are soluble in sodium chloride solutions. One of these globulins, *phaseolin*, probably forms about twenty per cent. of the seed, and has the following composition, which is the average of analyses of twenty-four different preparations:

| PHASEOLIN. | |
|----------------|--------|
| Carbon | 52.58 |
| Hydrogen | 6.84 |
| Nitrogen | 16.47 |
| Sulphur..... | 0.56 |
| Oxygen | 23.55 |
| | 100.00 |

This is the proteid described by Ritthausen in 1884, to which he assigned very nearly the same composition as that above given.

The other proteid, *phaselin*, is much more soluble, remaining in solution after the phaseolin has separated. It is slowly coagulated by heat at temperatures varying with the amount of salts present and the rapidity of heating. It is precipitated by acids, on prolonged dialysis yields insoluble or albuminate modifications, and has more nearly the properties of a globulin

¹ *Versuchs Stationen*, 39, 306.

than of any other recognized class of proteids. It has an unusually low nitrogen and high oxygen content as shown by the subjoined average of the analyses of eleven different preparations.

PHASELIN.

| | |
|----------------|--------|
| Carbon..... | 51.60 |
| Hydrogen | 7.02 |
| Nitrogen | 14.65 |
| Sulphur..... | 0.49 |
| Oxygen | 26.24 |
| | <hr/> |
| | 100.00 |

In addition to these two globulins, the extracts were found to contain an extremely small amount of *proteose*.

MAY, 1893.

A SAFETY ATTACHMENT FOR RIDERS.

BY CHAS. E. PARKER, PH.C.

Received August 30, 1894.

SOME years since, an attachment for manipulating the weighing rider of balances was introduced by Verbeck and Peckholdt. The arrangement, devised by the writer, and here described, appears to have some advantages in simplicity, lightness, and adaptability.

It consists of a piece of sheet brass cut in the shape shown in *b*, Fig. 1, to which is soldered a bit of hair-spring from a watch.

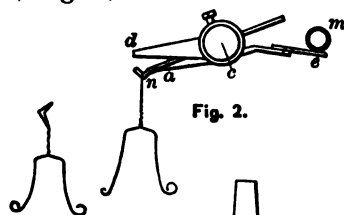


Fig. 2.

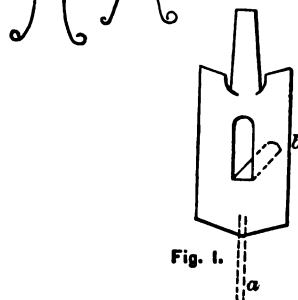


Fig. 1.

a; and of a light glass rod, *m*, Fig. 3, secured in a position parallel to the beam behind and slightly above it.

The piece of brass, *b*, is bent, as shown in Figs. 2 and 3, to form a sleeve upon the rod, *c*, together with a prong in apposition to the hook by which the rider is usually lifted, *n*, Fig. 2; and an extension, *e*, back under the rod, *m*, which thus limits the rotation of the sleeve and prong in one direction.

The operation is readily understood; the usual hook arrangement being converted into forceps

normally closed by the spring, *a*, thus securing the rider. When, by turning the rod, *c*, the rider is lowered, just before it rests upon the beam, contact between *m* and *e* checks the corresponding motion of the sleeve, thus opening the forceps; continuing

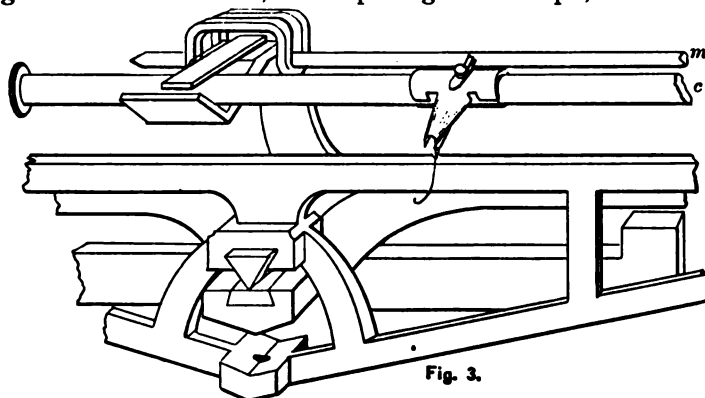


Fig. 3.

the movement, the rider is left hanging free upon the beam. Upon releasing the rod, *c*, the tension of the spring should be sufficient to close the forceps. When, however, it is often desirable to leave the rider upon the beam, by bending its loop, as shown in the side sketch, Fig. 2, this is easily effected.

Not the least advantage of this device is the readiness with which it can be extemporized.

ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE YELLOW PRECIPITATE.

By B. W. KILGORE.

Received September 15, 1894.

METHODS based upon the principle of titrating the yellow precipitate with standard alkali have been described by a number of chemists, especially for the estimation of phosphorus in iron and steel and their ores, where it is present in very small quantities. Among them may be mentioned by abstract:

E. Thilo (abstract *J. Anal. Chem.*, 1, part 2, 219, 1887) in the estimation of P_2O_5 in Thomas Slag, precipitates at $70^\circ C.$ with molybdic solution containing one part molybdic acid, three parts ammonium nitrate, and fifteen parts nitric acid, allows to stand five minutes, filters, washes with twenty per cent.

ammonium nitrate solution, and titrates with ammonium hydroxide and back with sulphuric acid.

C. E. Manby (*J. Anal. Appl. Chem.*, **6**, 82) precipitates near boiling, washes with three per cent. each nitric acid and potassium nitrate, dissolves in fifteen per cent. ammonium hydroxide, boils off the excess of ammonia, adds two cc. of nitric acid of 1.20 sp. gr., evaporates to dryness, heats sufficiently to expel nitric acid and ammonium nitrate, titrates with sodium hydroxide, and back with nitric acid.

J. O. Handy (*J. Anal. Appl. Chem.*, **6**, 204) precipitates at 85° C., shakes for five minutes, filters, washes five times with one per cent. nitric acid, five times with one per cent. potassium nitrate, and titrates.

M. Rothberg and W. A. Auchinvolle (*J. Anal. Appl. Chem.*, **6**, 243) precipitates at 40° C., shakes for one minute, allows to stand in a warm place five more, filters, washes five times with one per cent. nitric acid, five times with three-tenths per cent. potassium nitrate, titrates with sodium hydroxide, and back with nitric acid.

Dr. Franz Hündeshagen (*Chem. News*, **60**, 168, 177, 188, 201, 215) in his analytical studies of ammonium phosphomolybdate, shows its composition under all conditions, when free of molybdic acid and other impurities, to be $12\text{MoO}_3 \cdot \text{PO}_4 \cdot 3\text{NH}_4$.

He washes the precipitate with five per cent. solution of ammonium nitrate, titrates with sodium hydroxide, and back with nitric acid. He found that it required twenty-three molecules of alkali to neutralize one molecule of ammonium phosphomolybdate.

And H. Pemberton, Jr., (*J. Am. Chem. Soc.*, **15**, 382) has published the description of a method on this principle, which he applied to the determination of phosphoric acid in high-grade phosphates. He uses one-tenth gram substance for analysis, precipitates at boiling with aqueous ammonium molybdate, washes with water, titrates with potassium hydroxide, free from carbonates, and back with hydrochloric acid. In his first work, he found that it required 23.2 molecules alkali to neutralize one molecule ammonium phosphomolybdate, but in his later work he has obtained twenty-three molecules.

The writer has made quite a good many determinations of phosphoric acid in materials of varying percentages by this method, with fairly good results generally but with very wide variations at times, the tendency of the method being to give high results, although the yellow precipitate was washed liberally to remove free acid. It was believed that molybdic acid was the cause of the variations, as it was known that molybdic acid would deposit from other molybdic solutions very quickly at the temperature of precipitation used in the Pemberton method. To see if the aqueous molybdate was an exception to this rule, and also to see if the official molybdate of the Association of Official Agricultural Chemists would take the place of the aqueous solution, the official molybdate was used for precipitating at boiling temperature, the method as described by Pemberton being carried out otherwise, except that two-tenths gram of substance was used.

Results obtained in this way were less subject to variations than when the aqueous molybdate was employed, though high percentages would still often be obtained. Both molybdates were then tried side by side in the water-bath at temperatures of 70°, 65°, and 60° C., (this means practically 5° lower temperature in the beaker), allowing five minutes for precipitation, which was found in all cases to be complete. The results thus obtained were favorable to the lower temperature of 60° C. in bath and to the official molybdate, there being very few variations from the gravimetric method when precipitation was made at 60° C. and by official molybdate. A great many results were obtained in testing these and other points, but most of the early ones were not kept. In the following table are brought together some of the earlier results and all of the later ones by the volumetric method, either as carried out by Pemberton or myself or both, in the order in which they were obtained, and also results by the gravimetric method on the same samples for comparison. The gravimetric results were not duplicated. Among the earlier results by the volumetric method, there are quite a number of wide variations from the gravimetric results, but the later ones by the volumetric method as carried out by myself, nearly all show close agreement with gravimetric results.

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DETERMINATION OF PHOSPHORIC ACID IN VARIOUS FERTILIZERS BY
THE GRAVIMETRIC METHOD AND BY THE VOLUMETRIC
METHOD AS CARRIED OUT BY PEMBERTON
AND AS CARRIED OUT BY KILGORE.

| No. | Official. | Pember-
ton. | Kilgore. | No. | Official. | Pember-
ton. | Kilgore. |
|---------|-----------|--------------------|--------------------|---------|-----------|-----------------|--------------------|
| 1..... | 10.40 | | 10.34 ¹ | 35..... | 10.41 | | 10.26 ¹ |
| 2..... | 9.48 | | 9.40 ¹ | 36..... | 10.43 | | 9.46 ¹ |
| 2..... | | | 10.52 ¹ | 37..... | 12.26 | | 9.94 ¹ |
| 3..... | 2.44 | | 2.53 ¹ | 38..... | 8.83 | | 8.84 ¹ |
| 4..... | 2.85 | | 2.78 ¹ | 39..... | 8.11 | | 8.08 ¹ |
| 5..... | 3.90 | | 3.83 ¹ | 40..... | 13.36 | | 8.87 ¹ |
| 5..... | | | 3.80 ¹ | 41..... | 10.59 | | 10.34 ¹ |
| 6..... | 0.08 | | 0.30 ¹ | 42..... | 8.83 | | 8.56 ¹ |
| 7..... | 2.17 | 2.18 | | 43..... | 9.17 | | 9.26 ¹ |
| 8..... | 2.72 | | 2.62 ¹ | 44..... | 9.12 | | 9.17 ¹ |
| 9..... | 3.76 | 3.76 | | 45..... | 10.20 | | 10.33 ¹ |
| 10..... | 15.58 | | 15.48 ¹ | 46..... | 13.70 | | 13.62 ¹ |
| 10..... | | | 15.40 ¹ | 47..... | 13.92 | | 13.92 ¹ |
| 11..... | 14.09 | | 13.96 ¹ | 48..... | 15.75 | | 15.50 ¹ |
| 12..... | 13.61 | | 13.36 ¹ | 49..... | 8.14 | | 8.40 ¹ |
| 12..... | | | 13.60 ¹ | 50..... | 8.40 | | 8.22 ¹ |
| 13..... | 12.98 | | 13.06 ¹ | 51..... | 10.73 | | 10.80 ¹ |
| 14..... | 9.79 | 10.60 | 9.60 ¹ | 52..... | 9.63 | | 9.67 ¹ |
| 14..... | | | 9.70 ¹ | 53..... | 10.50 | | 10.48 ¹ |
| 15..... | 9.95 | 10.25 | 9.90 ¹ | 54..... | 10.53 | | 10.58 ¹ |
| 15..... | | 10.20 | 9.83 ¹ | 55..... | 11.13 | | 11.10 ¹ |
| 16..... | 1.25 | | 1.14 ¹ | 56..... | 8.96 | | 8.87 ¹ |
| 17..... | 2.64 | | 2.56 ¹ | 57..... | 10.75 | | 10.72 ¹ |
| 18..... | 1.68 | | 1.58 ¹ | 58..... | 10.73 | | 10.74 ¹ |
| 19..... | 4.06 | 4.05 | | 59..... | 11.63 | | 11.53 ¹ |
| 20..... | 2.07 | 2.10 | | 60..... | 9.59 | | 9.64 ¹ |
| 21..... | 1.37 | 1.31 ¹ | | 61..... | 13.96 | | 14.18 ¹ |
| 22..... | 2.14 | 2.19 ¹ | | 62..... | 14.43 | | 14.33 ¹ |
| 23..... | 1.30 | | 1.23 ¹ | 63..... | 14.37 | | 14.23 ¹ |
| 24..... | 3.93 | | 3.93 ¹ | 64..... | 10.67 | | 10.65 ¹ |
| 25..... | 10.90 | 10.87 | | 65..... | 9.49 | | 9.55 ¹ |
| 26..... | 11.28 | 11.90 ¹ | | 66..... | 10.61 | | 10.77 ¹ |
| 27..... | 8.89 | 10.55 | 9.00 ¹ | 67..... | 10.93 | | 11.11 ¹ |
| 28..... | 10.61 | 10.98 | | 68..... | 11.55 | | 11.59 ¹ |
| 29..... | 9.93 | 10.14 | | 69..... | 12.60 | | 12.45 ¹ |
| 30..... | 9.72 | 9.98 | | 70..... | 10.16 | | 10.45 ¹ |
| 31..... | 10.59 | 10.96 | | 71..... | 14.80 | | 14.77 ¹ |
| 32..... | 9.04 | | 9.10 ¹ | 72..... | 9.95 | | 10.20 ¹ |
| 33..... | 8.72 | | 8.72 ¹ | 73..... | 9.93 | | 10.22 ¹ |
| 34..... | 10.07 | | 10.00 ¹ | 74..... | 9.63 | | 9.80 ¹ |

ID BY TITRATION OF THE YELLOW PRECIPITATE. 769

| Official. | Pember-
ton. | Kilgore. | No. | Official. | Pember-
ton. | Kilgore. |
|-----------|-----------------|--------------------|-----------------------|-----------|-----------------|--------------------|
| 10.52 | | 10.49 ⁷ | 98..... | 9.76 | | 9.62 ⁷ |
| 11.00 | | 10.98 ² | 99..... | 11.26 | | 11.25 ² |
| 10.68 | | 10.71 ⁷ | 100..... | 11.49 | | 11.37 ⁷ |
| 13.42 | | 13.26 ⁷ | 101..... | 15.83 | | 15.73 ⁷ |
| 12.63 | | 12.60 ⁷ | 102..... | 15.71 | | 15.71 ⁷ |
| 15.06 | | 14.89 ⁷ | 103..... | 15.25 | | 15.20 ⁷ |
| 14.79 | | 14.84 ⁷ | 104..... | 11.64 | 12.15 | 11.63 ² |
| 14.87 | | 14.84 ⁷ | 105..... | 15.89 | 16.20 | 15.71 ² |
| 12.22 | | 12.17 ⁷ | 106..... | 15.54 | 16.15 | 15.65 ⁷ |
| 12.75 | | 12.72 ² | 107..... | 15.20 | 16.17 | 15.25 ² |
| 12.46 | | 12.34 ⁷ | 108..... | 13.96 | | 14.18 ⁷ |
| 11.23 | | 11.09 ⁷ | 109..... | 13.60 | | 13.67 ⁷ |
| 9.03 | | 9.12 ⁷ | 110..... | 15.67 | | 15.82 ⁷ |
| 10.49 | | 10.40 ⁷ | 111..... | 11.80 | | 11.85 ⁷ |
| 15.43 | | 15.30 ⁷ | 112..... | 11.74 | | 11.75 ⁷ |
| 16.27 | | 15.86 ⁷ | 113 ⁸ | 19.93 | 20.35 | 19.85 ⁷ |
| 15.98 | | 15.61 ⁷ | | 19.83 | 20.15 | 19.95 ⁷ |
| 15.71 | | 15.71 ⁷ | | 19.91 | 20.15 | 19.90 ⁷ |
| 11.83 | | 11.63 ⁷ | | 19.85 | 20.10 | 19.80 ⁷ |
| 10.04 | | 9.94 ⁷ | 114 | 17.17 | 17.20 | 17.15 ⁷ |
| 13.28 | | 13.25 ⁷ | | 17.12 | 17.40 | 17.10 ⁷ |
| 10.55 | | 10.42 ⁷ | 115..... | 2.42 | | 2.47 ⁷ |
| 10.41 | | 10.40 ⁷ | | | | |

ated at boiling.

ated in bath at 70° C.

ated in bath at 65° C.

ated in bath at 65° C. with the addition of five cc. HNO₃ to fifty cc. molybdic
sial).

4 with ten cc. HNO₃.

4 with three cc. HNO₃.

ated in bath at 60° C.

$2\text{HPO}_4 + 12\text{H}_2\text{O} = 19.826$ per cent. P_2O_5 .

are two main differences in the volumetric method as it by Pemberton and as carried out by myself. First, erature of precipitation in the former is at boiling; in 60° in bath or 55° C. in beaker. At the former tem-molybdic acid deposits very quickly, especially if any ble excess of the precipitant is present. If we know h phosphoric acid our samples contain and add just olybdate to do the work, or are willing to add little by he precipitating reagent till the proper amount has ed, this objection is largely overcome, but the former : know and the latter is tedious and time-consuming,

especially when large numbers of analyses are being carried on at once. At 55° C., the official molybdate does not deposit, at worst, for fifteen minutes or more; precipitation is always complete in four or five minutes from the time the molybdate is added, and precipitation and filtration can be finished in almost, if not in, as short a time by this method of procedure as by the regular Pemberton method, with the advantages of less danger of molybdic acid depositing, and of being able to handle a larger number of determinations at once.

The second difference is in the two molybdic solutions. The official molybdic solution contains practically sixty grams MoO_3 to the liter, and the Pemberton solution, sixty-six grams to the liter, so there is no very great difference in their precipitating powers. In the official molybdate the proportion of free nitric acid to molybdic acid is always the same, being equivalent to nearly fifteen cc. 1.42 sp. gr. acid to fifty cc. molybdic solution; while in Pemberton's molybdate the quantity is just five cc. 1.42 sp. gr. nitric acid, no matter whether twenty-five cc. or fifty cc. of the aqueous molybdate is added. It will be readily understood that should any considerable excess of this aqueous molybdate be added (and such a thing is liable to be done), and there being only five cc. nitric acid to hold it in solution, precipitation of molybdic acid would be sure and quick. To see which of the two molybdates was most liable to deposit molybdic acid under the same conditions, the conditions being as nearly as possible those of precipitation without the phosphate, the following experiments were made: Fifty cc. official molybdate, containing three grams MoO_3 , and fifteen cc. nitric acid were diluted with fifty cc. water; and to forty-five cc. of Pemberton's molybdate, containing 2.97 grams MoO_3 , were added, ten cc. saturated solution of ammonium nitrate, five cc. nitric acid, and forty cc. water. Both mixtures, being of the same volume and containing the same amount of molybdic acid, were placed in a water-bath at 60° C. The mixture of official molybdate showed no deposit for over twenty minutes, but a considerable one in one hour; the other mixture deposited seemingly the whole content of molybdic acid in less than four minutes and in fact this mixture could not be made to stand in the cold over three

or four minutes without throwing down great volumes of molybdic acid; but forty-five cc. and fifty cc. of the two molybdates are too much to precipitate the phosphoric acid from two-tenths gram substance, but not much in excess of safe quantities for most materials where four-tenths gram substance is used. With two-tenths gram substance, one-half the above quantities are about the right amounts to use. Experiments with them similar to the foregoing, were made as follows: Twenty-five cc. of official molybdate, containing one and five-tenths grams MoO_3 , and seven and five-tenths cc. nitric acid were diluted with five cc. water; and to 22.5 cc. of Pemberton's molybdate, containing 1.48 grams MoO_3 , were added five cc. nitric acid, ten cc. ammonium nitrate solution, and 12.5 cc. water. Both mixtures, being of the same volume and containing the same amount of molybdic acid, were allowed to stand as before. The mixture of official molybdate deposited about as in the first experiment; the Pemberton one remained clear for ten or fifteen minutes, when it commenced to get cloudy and in twenty minutes it was milky and a heavy deposit had formed. Seventeen cc. of the official molybdate and fifteen cc. of the Pemberton one contain the same amounts of MoO_3 , and when these quantities are used for precipitating equal amounts of nitric acid, five cc., are present in each case. When these amounts were diluted to fifty cc. and allowed to stand at 60°C . the deposits were the same as in the official molybdate in the two preceding experiments, which argues that the official molybdate contains about the right amount of nitric acid to prevent deposit of molybdic acid, and at the same time allow quick precipitation of phosphoric acid.

The aqueous molybdate as used in the Pemberton method works well when added in just the proper quantities, but there is not enough free nitric acid present to allow of much marginal excess. The official molybdate seems to contain a very large amount of free nitric acid. To test the effect of still larger quantities of free acid, the results in the table, as designated by the foot-notes, show that ten cc. additional nitric acid of 1.42 sp. gr. to fifty cc. molybdate hindered precipitation greatly; five cc. prevented its being complete in five minutes; while three cc. additional did not seem to interfere. The more free nitric acid

present, not to interfere with precipitation, the less liability there is of molybdic acid depositing. Just here I would add that the deposit from the official molybdic solution, at least, is not molybdic acid alone but a mixture of molybdic acid and ammonium molybdate. I found one deposit to contain 1.21 per cent. NH_3 .

The volumetric method as it has given me best results is as follows: Make solution as per the official nitric and hydrochloric acid method for total phosphoric acid, redissolve two grams substance in thirty cc. strong nitric acid and five to ten cc. hydrochloric acid, measure out twenty cc. for total or forty cc. for insoluble, corresponding to two-tenths and four-tenths gram substance respectively, into a four-ounce beaker, add ammonia till precipitate just begins to form, and dilute to seventy-five cc. If much of the nitric acid was driven off in making the solution add ten to fifteen grams ammonium nitrate, otherwise this is not necessary. Digest in water-bath at $60^\circ \text{C}.$ and after filtering the molybdate¹ used in the official method, precipitate in the usual way, allow to stand four or five minutes from the time the molybdate is added, filter as quickly as possible upon either a filter made by putting a platinum cone or disk, well filled with holes, into a three-inch funnel and covering with coarse asbestos, or upon the Hirsch funnel, or preferably upon a porcelain disk (the disk to be covered with filter paper) with rubber rim in three-inch glass funnel, using the pump in all cases. Wash the precipitate three to five times by decantation, using fifty to seventy-five cc. water each time and agitating thoroughly, then onto the filter and till no longer acid, titrate with potassium hydroxide and back with nitric acid.

N. C. EXPERIMENT STATION,
RALEIGH, N. C.

THE QUALITY OF WATER SUPPLIES.*

BY WM. P. MASON.

A PAPER of some length, bearing the title "The Quality of Water Supplies," has just been presented before the American Society of Civil Engineers, at their Niagara meeting, which contains considerable matter provoking comment. The

¹ This solution is made by dissolving 100 grams molybdic acid in 417 cc. 0.96 sp. gr. ammonia, and pouring this into 1,250 cc. 1.20 sp. gr. nitric acid.

² Read at the Brooklyn meeting August 16, 1894.

author appears to be a believer in the power of water to spread disease; but some of the statements and quotations advanced by him would certainly go far to unsettle the public mind and cause lack of faith in the teachings of some able masters.

He says: "While water is held to be a carrier of disease germs, the writer is not aware that any investigator has ever claimed to have seen these germs in water, even under the highest powers of the microscope; and the evidence that water is such a carrier of pathogenic bacteria is obtained by inoculation from water samples, of nutrient media in test-tubes or on culture plates. The typhoid bacillus in water has never been seen with the microscope without previous cultivation of the germ in nutrient media. Nor has it ever been demonstrated, so far as the writer is aware, that the presence of bacilli in water can be proven, excepting by delicate and difficult bacteriological processes."

That single individuals of the Eberth bacillus should escape direct detection is hardly to be considered surprising, in view of the enormous volume of water in which they are suspended. However difficult the processes of modern bacteriology may be for a tyro, it is hardly just to consider them unreliable in the hands of Koch, Pasteur, or Eberth; and if any one of these men, or of many other who might be named, should state that he had secured pure cultures of a specific germ, under circumstances which excluded the possibility of extraneous contamination, we should be exceedingly liable to believe him.

Again: "It is well understood that the infective element of typhoid fever can be present in water, and the chemical test be powerless to disclose it."

True enough! but it does not complete the story. The contaminated waters were pronounced pure. It must be remembered that the polluting material, as weighed, being very largely water, the pollution appeared greater than it really was. During an investigation following a serious outbreak of typhoid fever in the Tees Valley, England, the medical officer of the Local Government Board, London, caused preparation to be made of samples of pure water, to which small quantities (fifty and twenty-five parts per million) of typhoid dejecta had been added,

and these samples were then submitted to prominent water analysts for examination. No results upon which an adverse report could be based were obtained. Fifty parts per million of the typhoid dejecta corresponded to only four parts per million of total dry residue. As a natural result of these experiments, the purely chemical methods of water examination received very severe criticism, and the advocates of the exclusively bacteriological processes were correspondingly elated, for here were known instances of fatal contamination, which the chemists had failed to diagnose. Let this, however, be said in defense: In cases as they occur in practice, a serious addition of typhoid dejecta has much that is associated with it, of a comparatively inoffensive character, but which reacts with the chemical reagents, and tells the tale of sewage contamination, although the analyst can not venture to state the exact nature of the source whence the pollution is derived.

Not long since, the writer claimed that the river water furnishing a large Eastern city was contaminated with up-stream sewage, the opinion having been based not alone upon an analysis of the water at the intake, for the river was large and the consequent dilution great, but upon the difference between that analysis and one of the water taken from above the sewage inflow. The difference was small, but it was noticeable, and there was no other sufficient explanation of its existence than the one given. Later on, typhoid fever broke out in the upper valley, and epidemics developed not only in the city in question, but in all the neighboring towns using the river water for supply. Closely related cities and towns, which received their water from other sources, were not affected. Space does not permit of giving details, showing how clearly the case stood against the river water, but it is interesting to note that typhoid germs were most carefully sought for and were not found. That they were nevertheless present, there can be but little doubt.

Chemical analysis in this instance did certainly not detect the presence of typhoid, but what it did do, was to warn the people, months before the typhoid appeared, that they were drinking diluted sewage, and that they must beware of the time when that sewage came from pathogenic sources.

The paper in question goes on to say :

"The popular impression that the Koch or Finkler and Prior comma bacillus is the cause of cholera is fallacious, or, at least, not proven. The same remark applies to the typhoid bacillus of Eberth. The proof is still wanting that this will cause typhoid." This last is a quotation from Sternberg's *Manual of Bacteriology*, but it is very misleading because it is incomplete.

What Sternberg really says is this: "Recent researches support the view that the bacillus described by Eberth, in 1880, bears an etiological relation to typhoid fever; and pathologists are disposed to accept this bacillus as the veritable germ of typhoid fever, notwithstanding the fact that the final proof that such is the case is still wanting. This final proof would consist in the production of man, or in one of the lower animals, of the specific morbid phenomena which characterize the disease in question, by the introduction of pure cultures of the bacillus into the body of a hearty individual. Evidently it is impracticable to make the test upon man, and thus far we have no satisfactory evidence that any one of the lower animals is subject to the disease, as it manifests itself in man." Now that is a very different statement, and conveys a meaning greatly unlike the one suggested by the partial quotation referred to.

The paper says: Absolutely healthy persons have been known to reject the Eberth bacillus in their excrement, showing such, probably, to be in the intestines at all times." This is an error. To use the words of Sternberg, from whom the paper so often quotes: "No competent bacteriologist, so far as I know, has claimed to find the Eberth bacillus in the feces of healthy individuals."

As to the doubt thrown upon the correctness of the view that Koch's comma bacillus is the cause of cholera, the work of Sternberg will hardly endorse it. In this connection Sternberg says: "The etiological relation of this spirillum to Asiatic cholera is now generally admitted by bacteriologists," and also, "the most satisfactory evidence that this spirillum is able to produce cholera in man, is afforded by an accidental infection which occurred in Berlin in the case of a young man who was one of the attendants at the Imperial Board of Health when

cholera cultures were being made for the instruction of students."

As to the statement in the paper that "fatal cases of typhoid have been attended with none of the Eberth bacillus in the feces, or in the intestines, the seat of the disease," it is to be noted that Gaffky's investigations show it to be by no means a serious objection. He considers the technical difficulties surrounding a hunt for the bacillus in some few instances so considerable as to readily account for a small percentage of negative results, and he cites instances where he found the "germ" after an amount of patient search extending far beyond the point where the average observer would have ceased work and placed a negative report upon record.

Finally, the paper has much to say upon the imperfections of modern filters and the danger of using water therefrom. It goes without saying that pure water is better than purified water, but then the former is often unattainable, and we have to do with the latter or go without.

The paper lays especial stress upon the fact that even when the filtration is so successfully accomplished as to leave in the filtrate only one or two bacteria per cubic centimeter, yet "a person may imbibe from 250 to 500 bacteria in drinking a single glass of water, some of which may be pathogenic and produce typhoid fever, or some less dangerous disease." Such a degree of excellence in filtration as the obtaining of a filtrate with only one or two bacteria per cubic centimeter is indeed rarely attained, yet the public have a right to look with confidence upon a plant which does not pretend to accomplish half that amount of purification.

Consider for a moment what the Altona filters did for that city during the Hamburg cholera epidemic of 1892. The Altona water was taken from the Elbe river at a point below the outfalls of sewers carrying the cholera-infected sewage of 800,000 people. Yet Altona had but very little cholera (except imported cases), while Hamburg was scourged by it. The cities are practically one, a stranger being unable to tell the dividing line.

Take the numbers showing the efficiency of the Altona filters during one month of 1892:

The bacteria in the raw Elbe water per cubic centimeter varied from 9,370 to 44,140, with an average of 28,667. The average number in the filtered water was ninety. This meant a removal of 99.69 per cent. of germs of all kinds, 0.31 per cent. still remaining. The filtrate was by no means sterilized, but the city was protected from a cholera epidemic under circumstances trying in the extreme. As to the efficiency of sand filtration for water purification, the following figures are given for results found at the Lawrence experiment station, the filters having been operated with water containing known quantities of bacteria:

Rate in gallons per acre daily, 1,500,000; kind of bacteria added, *B. typhi. abdom.*; per cent. removed, 99.93; rate in gallons per acre daily, 3,000,000; kind of bacteria added, *B. prodigiosus*; per cent. removed, 99.95.

This reduction of the number of germs in a given volume of water is possibly equivalent to a dilution of the unfiltered water with a very large volume of a pure supply; and in this connection the writer of the paper says: "Dilution may reduce the chances of any single individual imbibing a fatal germ, but the germ itself will be just as dangerous when it is imbibed."

This is, doubtless, true if the individual be especially susceptible, for it has been experimentally shown that a single germ may produce fatal results when injected into an animal very prone to the special disease, but it has been also shown that when the animal is not very susceptible, the "dose" of bacteria has to be enormously increased to produce any result. We incline to believe that some similar reason may account for the apparent immunity of that fraction of a community, which has been equally exposed but which escapes contagion.

What the paper says regarding the unsatisfactory results observed where household filters are in use, is, unfortunately, very true, but the fault is more commonly with the attendant than with the filter. The common belief is that a filter, once established, is good for all time, and I could tell tales of what I have seen, in otherwise well-organized establishments, that would stagger belief. I do not approve of general household filtration, as I believe purification can be better and more cheaply done on

the large scale by the municipal authorities, but I can not think that the Pasteur filter should be swept aside like the worthless contrivance the paper calls it. My experience is that, with proper care, it is efficient. Extended tests were made with it for the Connecticut Board of Health in 1892, which show that it may be depended upon, if the porcelain cylinder be cleaned and sterilized once a week.

Freundenreich has obtained similar results, and has also shown that the length of time during which the filter is efficient depends upon the temperature.

RENSSELAER POLYTECHNIC INSTITUTE,
August, 1894.

THE PROTEIDS OF COTTONSEED.¹

BY THOMAS B. OSBORNE AND CLARK G. VOORHEES.

THE only reference to the proteids of cottonseed which we can find was made by Ritthausen in 1881 (*J. prakt. Chem.*, **23**, 485), who stated that he had been unable to obtain crystals of proteid matter from this seed and also that he would soon publish his complete investigations of the proteid bodies of this as well as of several other seeds which he named. Papers on the proteids of the other seeds mentioned by him were subsequently published, but we have not found anything relating to those of cottonseed. Since so long a time has elapsed, we feel warranted in assuming that Ritthausen has abandoned his intention of reporting the results of his investigation. The importance which cottonseed-meal has assumed as a cattle-food of late years, makes it desirable to understand its chemical composition, especially as regards the nitrogen compounds which it contains so abundantly. Our results are not as satisfactory as we hoped for when we undertook this work but we have decided to publish them as they stand and shall endeavor to make them more complete in the future. The difficulties encountered are due to the presence of substances which render filtration of the extracts extremely slow and to the large amount of coloring matters taken up from the seed together with the proteids, which could be separated only with difficulty and large loss of substance. The material used in our investigation consisted partly of seed

¹ First printed in the Report for 1893 of the Connecticut Agricultural Experiment Station.

from which the cotton had been removed, but which otherwise was in the condition in which it was harvested. We separated the kernels from these seeds by chopping them in a wooden bowl and sifting out the larger fragments of husk. We thus succeeded in obtaining meal nearly free from hulls. This meal was bruised in a mortar and freed from most of the oil by extraction with benzine and from benzine by drying in the air at the temperature of the room. Samples of commercial cottonseed-meal from which the oil had been expressed by the usual process were also used and gave the same result when extracted, and therefore in the following account of our experiments, no special mention is made of the origin of the meal employed.

a. Extraction with Water.—100 grams of cottonseed-meal were extracted with three liters of distilled water and the filtered extract saturated with ammonium sulphate. The small precipitate so produced was filtered off, dissolved in water, the solution filtered clear and placed in a dialyzer. After remaining a week in running water, no precipitation occurred, showing the absence of any notable quantity of globulin soluble in the dilute saline solution produced by the salts of the seed with the water used in the extraction. The dialyzed solution gave no immediate coagulum on boiling, proving the absence of albumens. The solution was then evaporated over a lamp and, after boiling some time, a light, bulky coagulum gradually separated. When the solution became quite concentrated, the coagulum was filtered off, washed with water, alcohol, and ether, dried over sulphuric acid and found to weigh 0.25 gram. The filtrate from this coagulum was evaporated to small volume on a water-bath and precipitated by pouring into absolute alcohol. The precipitated proteid was then washed with absolute alcohol and ether and weighed, when dry, 0.40 gram. Accordingly, 0.65 per cent. of the oil-free meal, consisted of water-soluble proteose-like matter. The amount of this substance was so small, and the difficulty of preparing it in a state of purity so considerable, that it was not further examined. Other experiments, both with water and saline solution, fully confirmed the results here described and left no doubt that the amount of water-soluble proteid is very small.

b. Extraction with Sodium Chloride Solution.—When treated with ten to twenty per cent. sodium chloride solution, the cottonseed-meal yields a slightly acid extract of a yellowish-pink color which is viscid, and difficult to filter. When heated slowly, this extract becomes turbid at 44°, flocks, in small amount, separating at 64°. Filtered after heating to 70°, the solution becomes turbid when heated again to 70° and flocks in larger amount separate at 93°.

Saturation with sodium chloride gives a slight precipitate. Dilution of the extract with water yields an abundant precipitate which is redissolved on warming and again separates in the form of spheroids when cooled.

Fifty grams of oil-free meal were extracted with ten per cent. sodium chloride solution, and the meal washed with the same solution as long as any proteid could be extracted. The extract and washings were saturated with ammonium sulphate, the precipitate produced filtered off, dissolved in dilute sodium chloride brine, filtered, and dialyzed four days. The solution was then removed from the dialyzer and the precipitated globulin filtered off, washed with water, alcohol, and ether, and dried over sulphuric acid. There was thus obtained seven grams or fourteen per cent. of light yellowish proteid which, when dried at 110°, had the composition given below, preparation 1.

A second preparation was made by treating 100 grams of meal with three liters of twenty per cent. sodium chloride solution for forty-eight hours and, after filtering, saturating the extract with ammonium sulphate. The meal-residue was again treated with twenty per cent. sodium chloride brine and after filtering the extract, it was saturated with ammonium sulphate and added to the first.

The ammonium sulphate precipitate was filtered off and dissolved in ten per cent. sodium chloride solution, yielding a deep brown liquid. This was filtered clear and dialyzed till free from chlorides when the precipitate was filtered off and treated in the usual way. There resulted 15.83 grams of globulin of a slightly yellowish color which had the composition stated below, preparation 2.

A third preparation was obtained by extracting 100 grams of

meal with water and then treating the residue with twenty per cent. sodium chloride solution.

The salt-extract was filtered, saturated with ammonium sulphate and otherwise treated in the manner already described in making preparations 1 and 2. Only 8.39 grams of globulin were recovered, indicating a conversion into the insoluble modification through contact with water.

The composition of this preparation 3, is shown by the following figures.

| COTTONSEED GLOBULIN. | | | | | | | | | | | |
|----------------------|--------|-------|-----------|-------|--------|-------|-----------|-------|--------|-----------|--|
| 1 | | | | 2 | | | | 3 | | | |
| | I. | II. | Ash-free. | | I. | II. | Ash-free. | | | Ash-free. | |
| Carbon..... | 51.85 | | 51.85 | 51.91 | 51.75 | | 51.75 | 51.86 | 51.66 | 51.77 | |
| Hydrogen.. | 6.78 | | 6.78 | 6.79 | 6.87 | | 6.87 | 6.88 | 6.73 | 6.74 | |
| Nitrogen... | 18.02 | 18.12 | 18.07 | 18.09 | 17.90 | 18.15 | 18.03 | 18.07 | 17.93 | 17.97 | |
| Sulphur ... | 0.68 | | 0.68 | 0.68 | 0.67 | | 0.67 | 0.67 | 0.71 | 0.71 | |
| Oxygen | | | | 22.53 | | | | 22.52 | | 22.81 | |
| Ash | 0.11 | | 0.11 | | 0.21 | | 0.21 | | 0.22 | | |
| | 100.00 | | | | 100.00 | | | | 100.00 | | |

The properties and composition of this substance are so similar to those of the vegetable vitellin found in the seeds of flax, hemp, wheat, and other seeds, it seemed probable that the three preparations just described were not entirely pure and that if freed from all foreign matters they would agree more closely with the globulin of the seeds just named. Three preparations were accordingly made, substantially in the manner already described and, after drying over sulphuric acid, they were redissolved in ten per cent. sodium chloride brine and the resulting clear solutions were dialyzed. The globulin thus reprecipitated, was filtered off, thoroughly washed with water, alcohol, and ether and when dried at 110° analyzed with the following results:

| COTTONSEED GLOBULIN. EDESTIN. | | | | | | | | | | | |
|-------------------------------|-----------|-------|-------|-----------|-------|-------|-------|-----------|--|-----------|--|
| 4 | | | 5 | | | 6 | | | | | |
| | Ash-free. | | | Ash-free. | | I. | II. | Ash-free. | | Ash-free. | |
| Carbon | 51.59 | 51.75 | 51.56 | 51.93 | 51.68 | 51.58 | 51.63 | 52.05 | | | |
| Hydrogen | 6.68 | 6.70 | 6.92 | 6.97 | 7.11 | 6.92 | 6.97 | 7.02 | | | |
| Nitrogen | 18.72 | 18.78 | 18.40 | 18.52 | 18.66 | 18.40 | 18.53 | 18.68 | | | |
| Sulphur | 0.75 | 0.75 | 0.50 | 0.51 | 0.66 | | 0.66 | 0.66 | | | |
| Oxygen | | 22.02 | | 22.07 | | | | 21.59 | | | |
| Ash | 0.33 | | 0.74 | | 0.82 | | 0.82 | | | | |
| | 100.00 | | | 100.00 | | | | | | 100.00 | |

We next attempted to detect the presence of other globulins in the sodium chloride extract. One kilogram of cottonseed-meal was extracted with ten per cent. sodium chloride solution and as the extract after straining through cloth was quite concentrated and could not be filtered, it was shaken with ether so as to remove oil and other substances soluble in that liquid. On standing, a part of the aqueous solution separated, leaving a supernatant layer consisting of an emulsion which long standing failed to resolve. Addition of alcohol, instead of breaking up the emulsion, transformed it into a jelly-like mass of considerable solidity. The unemulsified part of the extract, after standing some time, was decanted and dialyzed free from chlorides. The dialyzed solution was allowed to stand until the globulin had deposited when the supernatant liquid was decanted. The separated globulin was treated with ten per cent. sodium chloride brine and the solution filtered very nearly clear. This solution was then dialyzed for eighteen hours, during which time a large precipitate formed which was filtered off, washed with water, alcohol, and ether, and, when dried over sulphuric acid, weighed 23.63 grams, preparation 7. The filtrate was found to be practically free from proteids. The solution decanted from the first precipitation of the globulin contained a large amount of very finely divided substance that would not settle. A little sodium chloride was therefore added which dissolved the suspended globulin. The solution was next saturated with ammonium sulphate and the large precipitate filtered off, dissolved in water, the solution filtered perfectly clear, and dialyzed for several days. It was then removed from the dialyzer and allowed to stand until the suspended globulin had mostly settled out. The milky solution was then decanted from the sediment and the latter washed with water, alcohol, and ether. After drying over sulphuric acid it weighed 8.58 grams. Preparation 8. The solution decanted from 8, after repeated filtration was obtained clear and was again dialyzed. After several days a very small precipitate formed which, when subjected to the usual treatment, weighed but 0.82 gram. This was much colored and evidently impure. The solution filtered from this precipitate was saturated with ammonium sulphate and yielded

only a very small precipitate which appeared to consist mostly of proteose. The emulsion obtained by shaking the original extract with ether, after standing some days, gave no evidence of re-solution. The jelly-like mass was therefore broken up and thrown on a filter. A clear quick-running filtrate was obtained which was dialyzed for five days and deposited a globulin, that, after the usual treatment, weighed 8.43 grams. Preparation 9. All these preparations were analyzed with the following results:

| | COTTONSEED GLOBULIN. | | | | EDESTIN. | | | |
|----------------|----------------------|-------|-------|-----------|-----------|-------|-----------|-------|
| | 7 | | | | 8 | | 9 | |
| | I. | II. | Av. | Ash-free. | Ash-free. | | Ash-free. | |
| Carbon | 51.59 | 51.45 | 51.52 | 51.75 | 51.38 | 51.44 | 51.10 | 51.33 |
| Hydrogen | 7.04 | 6.70 | 6.87 | 6.90 | 6.70 | 6.70 | 6.88 | 6.91 |
| Nitrogen | 18.76 | 18.71 | 18.74 | 18.82 | 18.49 | 18.51 | 18.47 | 18.55 |
| Sulphur | 0.61 | | 0.61 | 0.61 | | 23.05 | 0.60 | 0.60 |
| Oxygen | | | | 21.92 | | | | 22.61 |
| Ash | 0.46 | | 0.46 | | 0.12 | | 0.46 | |
| | 100.00 | | | | 100.00 | | 100.00 | |

The above analyses show that the first three preparations were not quite pure and the extract, last made, affords satisfactory evidence that no other salt-soluble globulin exists in the cottonseed in noteworthy amount. In the following table, the analyses of the purer preparations may be compared together.

| SUMMARY OF ANALYSES OF COTTONSEED GLOBULIN. EDESTIN. | | | | | | |
|--|--------|--------|--------|--------|--------|--------|
| | 4 | 5 | 6 | 7 | 8 | 9 |
| Carbon..... | 51.75 | 51.93 | 52.05 | 51.75 | 51.44 | 51.33 |
| Hydrogen.. | 6.70 | 6.97 | 7.02 | 6.90 | 6.70 | 6.91 |
| Nitrogen... | 18.78 | 18.52 | 18.68 | 18.82 | 18.51 | 18.55 |
| Sulphur ... | 0.75 | 0.50 | 0.66 | 0.61 | 23.05 | 0.60 |
| Oxygen.... | 22.02 | 22.08 | 21.59 | 21.92 | | 22.61 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

The table subjoined shows that this substance agrees in composition with the vitellin which exists in the seeds of wheat, maize, hemp, castor-bean, squash, and flax. As the properties of the preparations obtained from all these sources are substantially alike, there can be little doubt that one and the same proteid exists in them all. For this body we adopt the name *Edestin*, from the Greek *εδεστος*, signifying edible, in view of its occurrence in so many important food-stuffs.

| COMPOSITION OF EDESTIN FROM VARIOUS SEEDS. | | | | | | | |
|--|------------------|------------------|----------------|------------------|-----------------|----------------|-----------------|
| | Wheat
kernel. | Maize
kernel. | Hemp-
seed. | Castor-
bean. | Squash
seed. | Flax-
seed. | Cotton-
seed |
| Carbon..... | 51.03 | 51.71 | 51.28 | 51.31 | 51.66 | 51.48 | 51.71 |
| Hydrogen.. | 6.85 | 6.85 | 6.84 | 6.97 | 6.89 | 6.94 | 6.86 |
| Nitrogen... | 18.39 | 18.12 | 18.84 | 18.75 | 18.51 | 18.60 | 18.64 |
| Sulphur ... | 0.69 | 0.86 | 0.87 | 0.76 | 0.88 | 0.81 | 0.62 |
| Oxygen | 23.04 | 22.46 | 22.17 | 22.21 | 22.06 | 22.17 | 22.17 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

The considerable differences in carbon and nitrogen in the above analyses amounting, in the extreme cases, to 0.7 per cent. are, in general, not greater than the discrepancies between analyses of preparations from the same seed. In the seeds of wheat and maize, other water and salt-soluble proteids occur in considerable quantities and it is probable that the crystallized preparations obtained from hemp, castor-bean, squash, and flax more truly represent the composition of edestin than the amorphous or spheroidal substance yielded by the cereal seeds.

The slight differences in the deportment of solutions of these preparations of edestin may be reasonably attributed to admixtures of traces of other proteids.¹

c. Extraction with Potash Water.—After extraction with water and sodium chloride solution a considerable amount of proteid was always found in the residual-meal which could be partly removed by two-tenths per cent. potash solution. All attempts to obtain the proteid thus extracted in a pure state, have hitherto entirely failed. Much coloring matter passes into the alkaline solutions, and when the proteid is precipitated, goes down with it and can not be removed by any process we have hitherto applied.

When freshly prepared, the alkaline extracts, as well as the meal moistened with the alkali, are of a bright reddish-yellow color, but on exposure to the air they rapidly darken and finally become greenish-black. So much gummy matter is also extracted by alkaline solutions that it is almost impossible to filter them clear. As a result no preparations were obtained, the analysis of which could shed any light on the composition of the proteid which they represented. The residue of meal after treatment with potash still contains a notable quantity of nitrogen.

¹ See paper on Crystallized Vegetable Proteids, by T. B. Osborne, *Am. Chem. J.*, 1688.

d. Amounts of the Different Forms of Proteids in Cottonseed.—

As already shown, the proteid matter of cottonseed soluble in water, consists almost wholly of proteose. Making full allowance for incomplete extraction and loss, this does not exceed 0.75 per cent. of the oil-free meal. The highest yield of globulin recovered in the preceding extractions was 15.83 per cent. of the oil-free meal, and contained 42.3 per cent. of the total nitrogen. After repeated extraction with potash water, the residue contained, in the case where extraction was most complete, 11.4 per cent. of the total nitrogen, showing that 88.6 per cent. of the total nitrogen had been dissolved. The difference between the percentage of nitrogen removed by sodium chloride solutions and that extracted by weak potash, represents the proteid dissolved by potash water which is not soluble in saline solutions, and which corresponds to 46.3 per cent. of the total nitrogen, assuming all this nitrogen to be present in proteid form.

These data may be tabulated as follows:

| | Per cent. of
Air-dry and oil-
free meal. | Total
nitrogen. |
|---|--|--------------------|
| Proteose..... | 0.75 | 2.0 |
| Salt-soluble proteid. Edestin..... | 15.83 | 42.3 |
| Alkali-soluble and salt-insoluble proteid. | | 44.3 |
| Proteid insoluble both in salt and alkali. | | 11.4 |
| | | 100.0 |

ON THE ANALYSIS OF AMERICAN REFINED COPPER.¹

BY HARRY F. KELLER.

IT is generally conceded that the presence even of minute quantities of other elements in metallic copper has a marked influence upon its physical properties, and especially upon its electric conductivity.

The copper produced in the Lake Superior region is relatively free from injurious admixtures, and is, therefore, generally preferred when a high conductivity is desired. "Lake" copper is always quoted a trifle higher than the metal from other localities.

Of late years the production of copper from impure sulphide ores has grown enormously, and, at the same time, the quality of the product has steadily improved. It has, indeed, become

¹ First printed in the Journal of the Franklin Institute, July, 1894.

possible through the introduction of the Manhés converter and the electrolytic process of refining, to obtain from matte a metal nearly, if not quite, as pure as the native copper of Lake Superior. Unfortunately, it appears that the very slight traces of the impurities retained in it affect the conductivity to a greater extent than is the case in the best lake copper. Silver and iron are the chief impurities of the latter, while electrolytic copper not infrequently contains small quantities of bismuth, antimony, arsenic, selenium, and tellurium.

That the exact manner in which these elements affect the physical properties of copper is not better understood, is, undoubtedly, owing to the lack of rapid, and at the same time accurate, methods of ascertaining their relative amounts. It is astonishing to note that the works on quantitative analysis, published in the English language, entirely neglect copper analysis. To my knowledge the important contributions to this subject by Hampe, Fresenius and other German chemists have not been translated.

For several years past I have given considerable attention to this subject. My analyses include the metal from the Lake mines, as well as copper obtained from Western mattes.

To the former, I found Hampe's original method¹ of analysis well adapted. This consists essentially in precipitating, by electrolysis, the greater part of the copper, and separating the metallic impurities in the usual manner from the remaining solution. The non-metallic elements such as oxygen and sulphur, are determined in separate portions of the sample.

For obvious reasons it is not desirable to employ this method in analyzing electrolytically refined copper. Accurate results can be obtained by following the plan proposed by Fresenius,² but the separation of large quantities of copper by means of hydrogen sulphide, and the difficulty of accurately weighing bulky solutions, render this method very objectionable. A far more convenient process is the one recently published by Professor Hampe.³ It is also more rapid than either of the two methods mentioned, and, with some modifications, it is especially

¹ *Ztschr. f. Berg. Hütten u. Salinenwesen*, 21, 218, and 22, 93.

² *Ztschr. anal. chem.*, 21, 229.

³ *Chem. Ztg.*, 1893, 92, 1691.

well adapted for the analysis of most of the American refined coppers.

The process depends upon the removal of most of the copper as cuprous sulphocyanate.

The manner in which I practice it is briefly as follows:

Twenty-five grams of material are placed in a tall, lipless beaker and treated with a mixture of 200 cc. of water, forty-five to forty-six cc. of nitric acid (sp. gr. 1.21), and twenty-five cc. of concentrated sulphuric acid (in case that much antimony or bismuth is present, as much as 100 cc. of sulphuric acid may be taken). The beaker is covered and heat applied until nitrous fumes are no longer given off and the solution then diluted with 200 cc. of water to prevent the separation of copper sulphate. A rapid current of sulphur dioxide is now conducted into the liquid, the temperature of which is maintained at about 40° C. When the nitric acid is destroyed and the red fumes have disappeared, the liquid becomes turbid, owing to the precipitation of silver, selenium, and tellurium. To insure the complete separation of the silver, a drop or two of hydrochloric acid may be added. After standing for twenty-four hours in a warm place, the solution is poured through a small filter into a graduated flask of two liters capacity. It may contain bismuth, antimony, arsenic, iron, nickel, and cobalt.

The sediment retained by the filter is composed of gold, silver, silver chloride, selenium, tellurium, possibly also lead sulphate, and traces of bismuth and antimony.

To determine the elements in the filtrate, the greater part of the copper must first be removed. To this end a measured amount of standard potassium sulphocyanate solution (one cc. = 0.05 Cu) is gradually added, whilst a current of sulphur dioxide is passed into the liquid. An excess of the sulphocyanate should carefully be avoided; it is preferable to leave some of the copper in the solution which should now emit a perceptible odor of sulphur dioxide. The delivery-tube is withdrawn and rinsed off into the flask, the contents of which are then made up to the mark. To effect a thorough mixing it is well to pour the contents into a dry beaker, and to retransfer them several times from one vessel to the other. The precipitate is allowed to set-

tle and an aliquot portion, say 1,800 cc. of the solution, filtered off. The separation and estimation of the different metals is effected according to the usual analytical methods. It is hardly necessary to state that the sulphur dioxide must be expelled before hydrogen sulphide is passed into the liquid.

In calculating the amounts of the metals contained in the entire liquid, we must allow for the volume occupied by the precipitate. According to Hampe, the specific gravity of the sulphocyanate is nearly three, and since twenty-five grams of copper would give about forty-eight grams of this salt, the volume of the latter would be sixteen cc. The actual volume of the solution, therefore, is $2,000 - 16 = 1,984$ cc. Suppose *e. g.*, we had filtered off 1,800 cc., and found in it 0.020 gram of arsenic, then

$$\frac{1984 \times 0.02}{1800}$$

would be the amount of arsenic in the sample taken.

There yet remains to describe the analysis of the insoluble portion from which the main solution was filtered. It may contain, as I have already said, gold, silver (both in the metallic state and as chloride), selenium, tellurium, lead sulphate, and traces of bismuth and antimony, occasionally also copper.

It is best to detach, as completely as possible, the dry mixture from the filter, and to destroy the latter with fuming nitric acid in a small porcelain casserole. The detached portion is then added, and treated with the nitric acid till completely oxidized. After evaporation on the water-bath of the free nitric acid, the residue is digested with dilute hydrochloric acid, which leaves the silver in the form of chloride. This is filtered off, purified, and determined in the usual way. From the filtrate, selenium and tellurium may be thrown down by means of hydroxylamine hydrochloride. In the cold this reagent seems to have little effect, but upon warming, a reddish turbidity is observed which gradually collects in the form of dark flakes. These represent all the selenium and tellurium; they are collected on a tared filter and dried at 105° – 110° C. to constant weight.

I have not been able to effect a clean separation of the two elements. Approximate estimations were made by fusing the

mixture in a current of hydrogen with potassium cyanide; the aqueous solution of the fused mass was then exposed to the air, which causes most of the tellurium to separate.

Gold, lead, and the traces of antimony and bismuth are determined by the ordinary methods.

NEW BOOKS.

SELECT METHODS IN CHEMICAL ANALYSIS, CHIEFLY INORGANIC, BY WILLIAM CROOKES, F. R. S., ETC., ETC.; EDITOR OF "THE CHEMICAL NEWS." Third edition, rewritten and enlarged; illustrated with sixty-seven wood cuts. London, and New York; Longmans. 1894. Price \$8.

This book is without padding and is but a bare, yet voluminous, statement of analytical fact. It is sufficiently explanatory to meet the wants of the average worker. It is minute in important details. It gives concise and clear, yet full, directions for separation and determination of all known elements, and has something to say of the hypothetical ones. And while but little is stated concerning those processes well understood by analysts, there is set forth about all which concerns the newer and verified ones. The book contains a skillful digest of the best of analytical literature down to the middle of the present year.

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possible of it; but he has a great deal more to say to him who desires a higher and better knowledge. He forgets how profoundly we are taught that matter is divided into common and rare elements. He keeps before him the necessity of giving to all forms of matter the same kind and quantity of study. Realizing that most rare elements are rare in quantity only, and that their distribution is indeed wide, he has given us the only English-written book to which workers in chemical and metallurgical technology can, under all circumstances, refer: workers whose necessities require that they shall be as familiar with many rare elements as they are with iron and with oxygen.

The great majority of American chemists regard Prof. Crookes as an honest and earnest and most consummate analyst. The small remainder, which does not so consider him, consists of those who do not know his work. One consults him with the comfortable feeling that his statements already are verified, that they have come out of his laboratory note-book, and that if possibly he should not give the solution of the problem in hand, he quite surely will teach enough to make the remainder apparent.

In the preface to this third edition, the author states that he desires the volume to be regarded chiefly as a collection of novel or little-known processes which have been found to be successful. He has not set himself the task of printing again that which may be found abundantly in special literature; except, that he has felt impelled to give to the world a series of electrical separations and processes. After a critical examination of the volume, the reader will emerge with a consciousness that the author kept to his assigned task and that his work was well done.

WILLIAM GLENN.

BALTIMORE CHROME WORKS,
October, 1894.

A CHEMICAL AND METALLURGICAL HANDBOOK. BY J. H. CREMER, M.E.,
and G. A. BICKNELL, B.Sc. pp. 280. Cleveland, Ohio: J. B. Savage.
Price, \$2.50.

This book contains 280 pages of information chiefly in notes and tables, which is of especial importance to iron chemists and metallurgists, and which any practical chemist or metallurgist

needs in a form convenient for reference. The extended and successful experience of the authors in the chemistry and metallurgy of iron is an assurance of reliability.

In the tables of logarithms and reciprocals, factors and logarithms for the calculation of analytical results, the specific gravity of solutions, and in the table giving the molecular weights, specific gravity, melting-points, boiling-points, and solubility of the principal inorganic compounds, chemists will find much useful information. The tables for the analysis of iron ores facilitate the calculation of phosphorus, silicon, and sulphur. Moisture tables are inserted for the calculation of the percentage of iron, silicon, manganese, and other constituents in the ore in its natural condition from analysis of the dried ore. As an example of the careful effort expended in the preparation of this book, the phosphorus table gives the percentage of phosphorus in pig-iron, from the percentage of phosphorus and the percentage of iron in the ore, for a difference of 0.001 per cent. from 0.001 per cent. up to 0.100 per cent. Other data include a table of fractional parts of numbers in tenths from one to eighteen for the calculation of phosphorus and silicon in an ore burden, and a table which gives the cost per unit of iron from the price and analysis of the ore in differences of one-half per cent., or iron from forty to seventy per cent.

For the convenience of metallurgists and prospectors in the field, a brief outline of the principal geological formations is included. The principal minerals are given with their chemical composition and physical properties. Other tables contain the amounts of limestone required to produce slags of different composition, the quantity of slag produced, and numerous other data that every blast-furnace manager must have constantly at hand. Brief notes on the properties and mutual relations of carbon, silicon, sulphur, phosphorus, and manganese in blast-furnace practice, contain much useful information. The book is well printed and neatly bound.

CHARLES F. MABERY.

NOTES.

Changes in Official Methods of Soil and Ash Analysis.—The following are the principal changes in methods of soil and ash analysis adopted at the last meeting of the Association of Official Agricultural Chemists:

1. A sieve with circular openings one-half mm. in diameter is to be used in preparation of the fine earth for analysis.

2. Moisture is to be determined in the air-dried, prepared sample by drying a weighed portion to constant weight in a water-oven, the water of which is kept briskly boiling.

3. The digestion is to be done in a flask provided with a return condensing tube and heated for ten hours continuously in boiling water; ten grams of soil and 100 cc. of HCl of sp. gr. 1.115 are to be used, and the solution is to be made up to 500 cc. and aliquots taken for analysis, except where the insoluble residue exceeds ninety per cent., in which case twenty grams are to be used with 100 cc. of acid. Larger quantities of soil may be used if the proportion of acid and amount of dilution be preserved.

4. The silica soluble in Na_2CO_3 solution is to be separated before the ignition of the "insoluble residue" in both ash and soil analysis.

The methods of analysis are essentially the same as those provisionally adopted for the past two years, but as they have been rewritten and revised, it is necessary to refer to the forthcoming proceedings for the details. The proceedings are now in the hands of the printer and will soon be ready for distribution.

The recommendation of the reporter, that the question of the determination of available P_2O_5 and K_2O in soils, particularly by the action of dilute organic acids, be made one of the subjects for investigation next year, was also adopted.

ALFRED M. PETER,

LEXINGTON, Ky., Oct. 3, 1894.

Reporter on Soil and Ash, A. O. A. C.

ERRATUM.—Page 650, October 1894, fifteenth line, for *Amelia* read *Amherst*.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

THE DETERMINATION OF PHOSPHORIC ACID BY THE
MOLYBDATE-MAGNESIA METHOD.

BY B. W. KILGORE.

Received September 15, 1894.

FOR the investigation of the official molybdate method as used by the American Association of Official Agricultural Chemists for 1894, three samples were sent to various agricultural and commercial chemists with instructions for analysis.

No. 1 was a mixture of cottonseed-meal and castor pomace, containing about two and one-half per cent. P_2O_5 .

No. 2 was an acid phosphate with about seventeen per cent. P_2O_5 .

No. 3 was a phosphate solution containing ten grams C. P. disodium hydrogen phosphate ($Na_2HPO_4 + 12H_2O$) to the liter, the theoretical percentage of P_2O_5 in this salt being 19.826.

The discussion, which will be made here, of this work will be confined to the results obtained on solution No. 3, as it was the only sample whose content of P_2O_5 was definitely known. Twenty-eight chemists reported thirty-four determinations on No. 3, the highest of which was 20.67 per cent., and the lowest 19.74 per cent., the latter being 0.086 of one per cent. below the theory, and the former 0.844 per cent. above. The average of all results was 20.09 per cent., or 0.264 of one per cent. above the theory; the variation between highest and lowest results was 0.93 of one per cent.; the variation below the theory was 0.086 and above the theory 0.844 of one per cent. Eighteen per cent. of the determinations were within 0.05 of one per cent. of the theory, thirty-six per cent. within one-tenth, and forty-four per

cent. within two-tenths. In the work on this sample a few analysts have gotten results reasonably close to the theory, a great many have varied widely from it, and nearly all have gotten high results, which brings me to the point to which I desire to draw especial attention, and that is the tendency of the molybdate-magnesia method to give high results, even when the greatest care is exercised as is reasonable to suppose was the case in this test work. I might add here that nearly all the chemists taking part in this work had had some years experience with the method, and those who had not, worked under good supervision.

The tendency of the method then, it seems, is for high results, and it is in order to ask where the trouble lies.

The phosphate solution sent out was precipitated directly with magnesia mixture by four chemists, when they obtained (1) 19.92, (2) 19.93 and 19.94, (3) 19.91 and 19.85, and (4) 20.03 and 20.05 per cent. P_2O_5 , against (1) 19.93 and 19.87, (2) 19.93 and 19.91, and (3) 19.93 and 20.06 by precipitating with molybdic solution first.

The results here by both methods of procedure, while slightly high, most of them, are practically the same whether precipitation was made direct with magnesia mixture, or previously with molybdic solution. This argues that the trouble is not in the molybdate precipitate or precipitation. The magnesium ammonium phosphate precipitate obtained from this sample in the usual way was, after washing, dissolved by one chemist in hydrochloric acid and reprecipitated with ammonia, when he obtained 19.80 and 19.81 per cent. P_2O_5 , while another added one gram citric acid to the alkaline solution in which the "white precipitate" is formed and obtained 19.83 and 19.83 per cent. P_2O_5 against 20.06 and 19.93 by the regular method.

The results by the last two methods of procedure are, while few, close to the theory and indicate that in the regular molybdate-magnesia method that either some of the magnesium of the magnesia mixture is thrown down as hydroxide and contaminates the precipitate, or else the magnesium ammonium phosphate formed under the conditions of precipitation, contains more than a normal amount of magnesium, and that by dissolving the "white precipitate" in hydrochloric acid and reprecipitating,

and also by the presence of citric acid in the solution where the "white precipitate" is formed, the trouble is prevented.

H. Neubauer¹ has shown that magnesium ammonium phosphate formed in solutions containing an excess of both ammonia and magnesium salt, which is the condition of precipitation in the method under discussion, contains more than a normal amount of magnesium. The writer has had magnesium of the magnesia mixture to deposit as hydroxide and contaminate precipitates where very large excesses of the magnesia mixture were used in strongly alkaline solution and on long standing, though little or no error is thought to be introduced by this latter cause where the prescribed amount of magnesia mixture is used and too long standing not allowed. It is to the excess of magnesium in the magnesium ammonium phosphate, we consider, that the high results by the molybdate-magnesia method are due.

The results upon which the foregoing discussion is based will appear in the proceedings of the A. O. A. C. in the "Report on Phosphoric Acid" made by the writer to that association at its recent meeting.

N. C. EXPERIMENT STATION,
RALEIGH, N. C.

ON THE GUNNING METHOD FOR TOTAL NITROGEN IN FERTILIZERS.

BY W. E. GARRIGUES.

Received September 26, 1894.

COMPARED to the Scovell-Kjeldahl nitrogen method, that of Gunning, modified to include nitrates, does not seem to have met with the favor that its cleanliness and simplicity would warrant. It is believed that this is, in the main, due to the lower results consequent upon the use of the latter process; hence the following record of an investigation of its merits.

The work was commenced by running parallel analyses on fertilizers of unknown composition, containing sodium nitrate, by both of the methods named. In each case the manipulation, adopted by the Association of Official Agricultural Chemists,

¹ Abstract *J. Chem. Soc., of London*, October 1893, 489.

was rigidly adhered to. The appended figures, being the results obtained, speak for themselves:

| Kjeldahl with
zinc dust.
Per cent. nitrogen. | Gunning with
sodium thiosulphate.
Per cent. nitrogen. | | |
|--|---|------|------|
| 3.01 | 2.40 | 2.40 | |
| 4.98 | 4.30 | 4.35 | 4.55 |
| 3.53 | 3.00 | 3.10 | 3.24 |
| 4.02 | 3.50 | | |
| 4.67 | 4.05 | 4.21 | 4.24 |

A sample was then prepared from pure sodium nitrate and tankage. The latter was valued by the plain Kjeldahl and Gunning methods and by soda-lime combustion, with the following results:

| Kjeldahl. | Gunning. | Soda-lime. |
|-----------|----------|------------|
| 7.05 | 7.05 | 7.08 |

The calculated content of the mixture was 8.97 per cent. nitrogen, about one-half of which was in the inorganic form. On submitting this to analysis there were obtained:

| Kjeldahl. | Gunning. |
|-----------|----------|
| 8.90 | 7.17 |
| | 7.31 |
| | 7.46 |

It was very evident that in the writer's hands the Gunning method, as adopted by the Association, did not convert all the nitrogen present into ammonia. After numerous and varied experiments, which, as is usual when viewed in the light of foregone events, now seem to have been largely unnecessary; successful results were finally obtained by using the same reagents, both kind and quantity, but varying the mode and order of their addition.

For convenience of reference the official directions from Bulletin 38, U. S. Dept. of Agriculture, are here given:

"In a digestion flask holding from 250 to 500 cc. place from 0.7 to 2.8 grains of the substance to be analyzed according to the amount of nitrogen present. Ten grams of potassium sulphate, five grams of sodium thiosulphate, and thirty to thirty-five cc. of the salicylic acid mixture, *i. e.*, thirty cc. of sulphuric acid to one gram of salicylic acid, are then added and the whole digested at a low temperature until frothing ceases."

The above unsatisfactory, or rather useless, results were

obtained in this manner. The chief fault is in the addition of potassium sulphate at such an early stage in the process; the large quantity of dry powder forming an effectual blanket over the sample, that for some time resists the permeation of the viscid acid solution.

The best procedure was found to be: Adding the salicylic acid mixture directly to the sample in the flask, which is then shaken until the liquid has thoroughly wetted the dry organic matter, allow to stand about fifteen minutes, and add the thio-sulphate with constant shaking. This should be done in four or five portions, following with a fresh crystal only when the one previously added has completely dissolved. The potassium sulphate is then put in and the whole again well agitated. Digest as usual.

Handled in this manner the known mixture above referred to, gave:

8.85
8.87
8.90
8.92

Another sample of dry bone tankage and sodium nitrate was prepared and passed several times through a sixty mesh sieve. The tankage was valued as before, and showed:

| Kjeldahl. | Gunning. | Soda-lime. |
|-----------|----------|------------|
| 4.32 | 4.32 | 4.39 |
| 4.40 | 4.42 | |

The calculated content of the mixture was 6.49, and the analyses returned:

| Kjeldahl. | Gunning. |
|-----------|----------|
| 6.45 | 6.43 |
| | 6.45 |
| | 6.45 |
| | 6.46 |

Neither method gave results sufficiently accurate for the valuation of sodium nitrate alone; a carefully prepared sample of that salt showing on analysis:

| Kjeldahl. | Gunning. |
|-----------|----------|
| 16.05 | 15.80 |
| 16.35 | 16.00 |
| | 16.15 |
| | 16.22 |
| | 16.38 |

Theory 16.49

It will be noticed that without a single exception the returns of analyses were below the amount actually present. No means of avoiding this loss were found. It would, therefore, seem justifiable to report the highest figure in closely agreeing duplicates instead of the customary average.

Several blanks run through to determine the freedom from nitrogen of the reagents employed, gave from nil to 0.05 per cent. No corrections were made for this.

During the distillation in the Gunning process the solution frequently foams badly; so much so that unless the flame is turned very low, the froth rises into the connecting bulb. The addition of paraffin wax does not always overcome this difficulty, and to avoid it, the use of an ordinary thirty-two-ounce wash-bottle, in place of the 500 to 600 cc. distillation flask is recommended.

There is little doubt that the seat of responsibility for many minor discrepancies is imperfect prepartion of the sample. Attendant upon the use of the official twenty-five mesh sieve, variations in the hands of the same manipulator frequently reach 0.15 per cent., even when exceptional care is exercised. It has, therefore, been found advisable in nitrated goods to quarter down the twenty-five mesh sample to about two ounces and pass that through a sixty mesh sieve; when this is done, the difference in duplicate analyses rarely exceeds 0.05 per cent., and decinormal acid and alkali often fail to show any.

Occasionally it becomes necessary to dry the sample before it can be thus finely powdered; in that case making the moisture determinations of Stillwell and Gladding (Bull. 38, p. 19, U. S. Dept. of Agr.) is the best procedure, *i. e.*, weigh out a portion of about ten grams from the original package when first opened, and determine the total moisture in a water-oven, dry the remainder of the sample to dustiness, and prepare it as above; then weigh out two grams of the fine sample simultaneously with the portion to be used for nitrogen, and ascertain the remaining moisture. A simple calculation brings the nitrogen figure back to the original condition of the goods.

Usually, however, nitrated fertilizers contain only a few per cent. of moisture, as indeed they should, lest the free acid of

the phosphate in the presence of water, act on the easily decomposable salt and liberate nitric acid. This theoretic action has been found a sad reality by manufacturers who incorporated nitrate salts with a wet "super," the loss of plant food being accompanied by a destruction of the fiber of the bagging containing the goods.

FALLACIES OF POST-MORTEM TESTS FOR MORPHINE.¹

BY DAVID L. DAVOLL, JR.

Received August 9, 1894.

IN the qualitative investigations upon morphine in a former series of experiments, the tissue was allowed to putrefy in the open air, a condition which is not present in the case of a buried body, for in the unopened cadaver, the bacterial products are very different in their deportment toward certain reagents, from those formed by aerobic germs and are the interferences which would be met with in chemico-legal work and which give some of the tests for morphine.

The writer, during the spring of 1893, in a series of determinations to ascertain the minimum of loss entailed in the recovery of a weighed amount of commercial morphine sulphate—the form generally employed in instances of poisoning—from a given amount of putrefied tissue, obtained the following results by the method given in detail below:

A. From sixty grams of stale bread, containing 0.2387 gram of morphine sulphate, 0.0844 gram of anhydrous alkaloid were recovered, the equivalent of 0.2245 gram of morphine sulphate; this shows a loss of 0.0142 gram or 5.94 per cent. By qualitative tests upon $\frac{1}{800}$ part of this recovered amount, very decided affirmative results were obtained.

B. From 100 grams of fresh liver, containing 0.3455 gram of morphine sulphate, 0.1163 gram of anhydrous alkaloid were recovered, the equivalent of 0.3093 gram of morphine sulphate, a loss of 0.0362 gram.

C. From putrid liver (after standing ten days in the open air and in a warm place) charged, when fresh, with 0.442 gram of morphine sulphate, 0.111 gram of anhydrous alkaloid were

¹ Read at the Brooklyn Meeting of the American Association for the Advancement of Science. August, 1894.

recovered, corresponding to 0.2952 gram of morphine sulphate, a loss of 0.1468 gram.

After much experience with quantitative methods now in vogue, both in opium assay, and toxicological work I have used the method of titration of the alkaloid by standard acid and alkali, isolating the alkaloid by shaking out with primary amyl alcohol.

A careful review of the qualitative tests for morphine was first gone over, working with normal and decinormal solutions of the anhydrous alkaloid, in the form of sulphate. The figures here given, refer to the anhydrous alkaloid evaporated to dryness upon one spot in a porcelain dish.

Fröhde's Reagent.—See discussion below.

Iodic Acid, with starch paste, is sensitive to 0.00001 gram.¹

Nitric Acid, gives deep orange color with 0.00001 gram. This reagent also produces a red coloration with certain volatile oils and resinous substances.

Ferric Chloride, in neutral solution gives deep blue color, said by Wormley to be sensitive to $\frac{1}{100000}$. Results with putrefactive tissue are given below by the writer.²

Ferric Chloride with *Potassium Ferricyanide*, is sensitive to 0.000005 gram.³

Tattersall's Test, with sodium arsenate, followed by other reagents, is very satisfactory. (For details, see "New Color Reaction for Morphine, Codeine, and Atropine," *Pharm. J. Trans.*, [3], 12, 459-60.)

Many other tests were worked upon, but being for the most part confirmatory and quite intricate in their manipulation, they

¹ Blyth, 1885; Separation of Morphine from Animal Tissue and Fluids; Poisons, their Effects and Detection, 1, 278. Selvin has pointed out that amyl alcohol extracts from putrefied matters, "ptomaines," agreeing with morphine in setting free iodine from iodic acid.

² T. G. Wormley, 1885; Morphine, Micro-Chemistry of Poisons, second edition, 485-6, says "that the blue color produced by FeCl_3 upon morphine is discharged by free acids, caustic alkalies, and heat. The blue color may not make its appearance if foreign substances be present and it is open to fallacy."

³ O. Hesse, Morphine, *Pharm. J. Trans.*, 18, 801, says, "In the ferric chloride and potassium ferricyanide test for morphine, the action is due to the formation of pseudo-morphine and potassium ferrocyanide.

$8\text{C}_{17}\text{H}_{19}\text{NO}_2\text{HCl} + 8\text{K}_3\text{Fe}(\text{CN})_6 = 4\text{C}_{34}\text{H}_{38}\text{N}_2\text{O}_6 \cdot 2\text{HCl} + 6\text{K}_4\text{Fe}(\text{CN})_6 + 2\text{H}_4\text{Fe}(\text{CN})_6$. Pseudo-morphine is actually deposited if the solution is not too dilute and this substance being somewhat soluble in water, is the cause of the blue coloration."

were not applied in this work for reasons which the decisive results render obvious. The negative results in testing for morphine have always been regarded as more conclusive than the positive.

The object of this work was to demonstrate, as far as possible, to just what extent cadaveric alkaloids might respond to the generally recognized tests for morphine; and to this end, the ordinary manner of burial of a corpse was followed, and after exhumation the several parts of the body were subjected to exactly the same treatment that would be followed were morphine suspected to be present as a result of poisoning.

A collie (dog) was taken, weighing thirty-four avoirdupois pounds; was shot between the eyes on March 3rd, at 1.30 P. M. and placed in a tight pine-box, when the cover was screwed on. This was buried under five feet of soil, consisting of clay mixed with gravel, on the forenoon of March 5th. When buried, the body had already begun to give off a strong odor. The body was taken up on the morning of April 26th, after forty-five days burial, the usual spring weather intervening, the box being dry inside. Eight hours after disinterment, all the parts—portion of brain, heart, lung, kidney, liver, spleen, bladder and urine, stomach and contents, piece of intestine with contents—were separately macerating in diluted alcohol.

The weights of the several parts in grams were as follows: Brain, 45; heart, 173; lung, 200; kidney, 70; liver, 345; spleen, 28; bladder and urine, 105; stomach and contents, 450; intestine with contents, 130.

The odor from the opened cadaver was overpowering, particularly from the cranial cavity. All organs were soft, but retaining their form. The brain was of a semi-fluid consistence, and when, later, the liquid extract was shaken out with immiscible solvents it emulsified exceedingly.

The method of extraction, given below, includes some few modifications over the older method, none of which, however, were introduced without previous proof of their applicability to the recovery of the alkaloid, morphine. For convenience of reference in the following comments, the manipulation was divided into arbitrary stages, designated by Roman numerals.

I. The finely divided material is placed in a flask of suitable capacity, from which extends upward a glass tube, three and one-half feet long by one-fourth inch internal diameter; the arrangement provides for the constant alcoholic and acidulous strength during extraction, by air condensation. Enough diluted alcohol (by volume) is added to well cover the material and the mass made slightly acid with acetic acid. The digestion is made upon a long iron plate, heated by means of Bunsen burners, so placed, at intervals, that the flame should strike *between* the flasks and not *directly beneath* them. The flasks are placed in a row upon the hot plate, and further protected from direct heat of the iron plate by interposing match-sticks between the flask-bottom and the hot plate, and are virtually heated by hot air and not by the plate, the wood being such a non-conductor of the heat. The digestion is continued for one hour, the temperature, 70° C., being read from a thermometer immersed in the viscera. Then cool, remove to a funnel and filter through paper by means of a filter-pump, or strain through carefully washed muslin, rinsing the flask with successive small portions of diluted alcohol and passing washings through the tissue, previously well drained. Remove the mass to the extraction apparatus and repeat the process of extraction and filtration as before. Three extractions are accounted sufficient.

II. The alcohol is removed by evaporation upon the water-bath, stirring to promote vaporization and prevent the formation of a crust.

III. The measure of the residual aqueous liquid is now ascertained, and being of a sirupy consistence, is placed in a flask of suitable capacity and three volumes of ninety-five per cent. alcohol added; the evaporating dish is rinsed with seventy-five per cent. alcohol and the washings added to the liquid under analysis. Sulfuric acid, approximately fifty per cent., is added to slight acidulation and all is set aside for eight to twelve hours, agitating occasionally. It is then filtered by means of a filter pump, and the precipitate washed with successive small portions of seventy-five per cent. alcohol.

IV. Remove the alcohol from the filtrate by evaporation upon the water-bath, and dilute with just sufficient water to obtain a

limpid consistence. The presence of much fatty matter may necessitate filtration; maintain the acid reaction.

V. The acidulous solution is now shaken with successive small portions of water-washed chloroform, until, upon evaporation, the chloroform solution leaves no appreciable residue; the miscibility of the so-called immiscible solvents causes a slight residue to remain upon evaporation, even after the chloroform has performed its work.

VI. Now shake out the acidulous solution with a cold amyl alcohol. These two solvents (V and VI) remove coloring and fatty matter. The chloroform and amyl alcohol washings should be shaken with slightly acidulated water and this latter added to the original liquid under analysis.

VII. The liquid is now made alkaline with ammonia water of sp. gr. 0.962 at 15° C. and shaken out with several successive small portions of chloroform and ether (three parts to one), this to remove cadaveric alkaloids as much as possible; this was suggested by the solubility of the cadaveric alkaloids in these media and the insolubility of the morphine in the same. This is repeated four times, the aqueous liquid being each time acidulated, the immiscible solvent added, shaken, and again rendered alkaline before the solvent has time to separate into a layer; this is done in order to obtain the alkaloids nascent.

VIII. (a) The same conditions of acidulating, adding hot solvent and making alkaline were observed here as in "Stage VII." The suspected (acid) is heated to 70° C., placed while hot in a separatory-funnel, and when alkaline, shaken out with successive small portions of hot amyl alcohol, until a small portion, upon evaporation, gives negative results with some delicate test, three to five shakings being generally enough.

(b) The amyl alcohol solutions are mixed, filtered, and then shaken with successive very small portions of water until no precipitate is afforded with barium chloride.

IX. It is then evaporated to dryness upon the water-bath and the residue taken up with slightly acidulated water, fiftieth normal sulphuric acid being the strength employed.

X. Filter this liquid, heat to 70° C., and shake with two successive portions of hot amyl alcohol in *acid* solution, mixing the

amyl alcohol washings and agitating with a little acidulated water, which is added to the liquid under analysis. This is done to further remove coloring matter. See remarks further on.

XI. Heat again to 70° C., add hot amyl alcohol, shake, render alkaline with ammonia water (0.962), again agitate and remove the amyl alcohol solution; repeat this extraction with hot amyl alcohol until all the alkaloid has been removed. Now repeat the shaking with water, as mentioned in "Stage VIII (b)" in order to remove ammonium sulphate.

XII. Four-fifths of the final purified amyl alcohol solution are evaporated to dryness upon the water-bath and titrated with fiftieth normal potassium hydroxide and sulphuric acid, using cochineal solution as indicator. The remaining one-fifth is tested qualitatively by all reliable methods.

The above is a detailed account of the method of extraction.

Guareschi and Mosso found commercial alcohol almost invariably to contain small quantities of an alkaloidal substance, having an odor similar to that of nicotine and pyridine. In amyl alcohol, Haitinger has found as much as one-half per cent. of pyridine. The ethyl alcohol and primary amyl alcohol used in this investigation were purified by distillation over tartaric acid, using five grams of acid to each 100 cc. of alcohol, the distillates coming over at 78° and 130° respectively. The basic substance which exists in some samples of ether is pyridine. The ether was water-washed, dried over calcium chloride and redistilled. Ether containing alcohol, as is well known, has a tendency to remove morphine from alkaline media. The chloroform was water-washed and redistilled. None of the above enumerated solvents, upon evaporation of fifty cc., yielded any appreciable residue, and upon applying reagents for morphine to the spot upon which the evaporation had been made, entirely negative results were obtained. "Stage VI" was omitted in extraction of all parts, excepting with liver, kidney, and intestines, since it was thought that, as morphine is removed from acid solution by amyl alcohol, it would be advisable to first purify the alkaloid by stages VII and VIII, thus leaving much coloring and extractive matter behind, and then to shake out the *hot* acid solution with successive portions of hot amyl alcohol, where a less amount

of the solvent need be employed and at the same time the very objectionable coloring matter would be more thoroughly removed. It was noticed in "Stage VI" that the *cold* amyl alcohol removed very little coloring matter, but that this same solvent, when *hot*, removed very much in "Stage VIII," which is avoided in "Stage XI." The reason why this method was not employed in the cases of the liver, kidney, and intestines, was that the idea did not suggest itself until after the final tests were applied to these. Before making this departure from the usual method the feasibility of it was first to be ascertained by actual experiment. One-half the final purified extractive matter from the liver was taken, in which negative tests for morphine had been obtained by Fröhde's reagent, Le Fort's test, and ferric chloride. Into this extract was introduced 0.0006 gram of morphine and all evaporated to dryness upon the water-bath; taken up with 100 cc. of fiftieth normal sulphuric acid, and this *hot* solution (acid) shaken out with twenty-five cc. of hot amyl alcohol. The solution was now shaken out with successive portions of twenty-five, twenty, and twenty cc. of *hot* amyl alcohol in alkaline media. The final measure was sixty cc. of purified amyl solution, each cubic centimeter of which *could not* contain more than 0.00001 gram of morphine. One cc. of this solution evaporated to dryness upon one spot gave very decided tests for morphine by Fröhde's reagent, which was the only test applied to the only perceptibly yellow residue. This test was as pronounced and strong as from 0.00001 gram of morphine evaporated from aqueous solution.

The stomach and heart yielded an extract of a very dark color, but by subsequent purification, particularly at "Stage IX," it was reduced to a very pale yellow, and, in fact, all extractive matter was freed from almost all color at this point, as the fiftieth normal sulphuric acid failed to appreciably effect the dark residue left at this stage. This residue needs some further mention; it was brownish to black in color, somewhat resinous and plastic in consistence; when not abundant it appeared as a brownish cryptocrystalline residue, taken up to a considerable extent by the fiftieth normal sulphuric acid. By computation it will be seen that 100 cc. of fiftieth normal sul-

phuric acid is capable of saturating 0.57 gram of anhydrous morphine, $C_{17}H_{19}NO_5$; or 0.606 gram of crystallized alkaloidal morphine, $C_{17}H_{19}NO_5 \cdot H_2O$, corresponding to 1.516 grams of morphine sulphate, $(C_{17}H_{19}NO_5)_2H_2SO_4 \cdot 5H_2O$.

After treating with fiftieth normal sulphuric acid the solution is filtered through paper.

The final purified solution treated as above, is almost colorless at "Stage XII," and the residue left upon evaporation was, in the case of the brain, almost colorless: light yellow with all others, excepting the heart and stomach, which were yellow to light-brown.

The filtered liquid, after performing "Stage IX," was tested for alkaloids by bromine water, Wagner's solution, Mayer's reagent, sodium phosphomolybdate, and picric acid and all parts of the viscera gave strong precipitates with each reagent, excepting picric acid. The cautious addition of ammonia water to them also gave cloudiness.¹

The reagents for the final identification tests were prepared for the most part after the directions given in "Reactions" by F. A. Flückiger, translated, revised, and enlarged by J. B. Nagelvoort.² Fröhde's reagent was made of the strength 0.010 gram of molybdic acid to each cubic centimeter of sulphuric acid, sp. gr. 1.84, and dissolved by digesting below 150° C.

The nitric acid test, ferric chloride with potassium ferricyanide, and the ferric chloride test were of the above recognized strength (Flückiger).

Le Fort's test was applied as follows: Iodic acid in solution is applied to the dry residue and all intimately mixed; chloroform, in successive small portions, is floated over this until it ceases to remove the pink color of iodine, the chloroform solution being removed by absorption with filter paper; one drop of ten per cent. ammonia water (or until alkaline) is now added and morphine will give a deep "mahogany color" not affected

¹ For a discussion of the production of precipitates with organic matter by such general alkaloidal reagents as Wagner's solution, Mayer's reagent, bromine water and picric acid. See T. G. Wormley, 1885; Morphine, *Micro-Chemistry of Poisons*, second edition, 492.

² Schön, *Ztschr. anal. Chem.*, 8, (1869), 379., in regard to preparing Fröhde's reagent says: "A moderate heat only should be applied, since the molybdic acid is reduced to a blue precipitate by heat alone at the temperature of incipient vaporization of H_2SO_4 ."

by chloroform, but changing back to yellow with hydrochloric acid. 0.00001 gram of pure morphine will respond to this test but the writer would not claim such extreme delicacy of reaction in presence of foreign matter; 0.00005 gram gives a good decided test, suitable for recognition in recovered matter.

After somewhat extended work upon morphine in the viscera, it seems to me that under the conditions mentioned, Fröhde's reagent, Le Fort's test, and ferric chloride are the least fallacious of all recognized tests applied.

Fröhde's reagent is especially satisfactory, appearing immediately as a deep purple color, fading to violet, then green, when applied to extractive matter *known* to contain morphine, and under these conditions sensitive to 0.00001 gram. In applying this test two samples, each containing extract from two cc. of the purified amyl alcohol solution were evaporated upon one spot in a porcelain dish upon the water-bath; to one of them was first added, and intimately mixed, 0.00001 gram of alkaloid morphine; the test was applied to both samples at the *same time* and in no instance was there obtained any indications whatsoever of morphine in the sample of extract *not* containing that alkaloid, a light green color only, appearing; but, on the other hand, the sample to which 0.00001 gram of morphine *had* been added, never failed to give a decided purple color *immediately*. These parallel tests were made for the purpose of verifying the conclusion, that, had morphine (or an alkaloidal base acting similarly toward Fröhde's reagent) been present in even so small an amount as 0.00001 gram a reliable test would have been obtained.

With ferric chloride, freshly dissolved and free from acid, the same parallel tests were made as with Fröhde's reagent, with the exception that 0.00005 gram of morphine was introduced in the comparative test, since this test is not as delicate as the molybdate in extractive matter. When applied to the extractive to which morphine had been added, bluish rings appeared, a positive test; but with the pure extract, from all parts of the viscera, no color appeared.

Le Fort's test was applied with a parallel test, containing 0.00005 gram of morphine and was very satisfactory as a reagent,

and as far as demonstrating the absence of morphine or any interfering bases was concerned, was conclusive. With the extractive to which morphine *had* been added, a final "mahogany color" had been obtained, but no change with the pure extract from the parts of the body.

Iodic acid gave indications of a reducing agency, since iodine could be detected with clear, fresh starch-paste in all instances.

The nitric acid tests were found to be of no value, ferric chloride, with freshly prepared solution of potassium ferricyanide, gave indications of a base having similar reducing action as morphine. Parallel tests were made, the one containing the extractive from two cc. of final amyl alcohol solution, was evaporated to dryness, taken up with four cc. of fiftieth normal sulphuric acid; the other treated in an exactly similar way, *but* to which had been added 0.00001 gram of morphine. To both these solutions were added eight cc. of a solution of potassium ferricyanide and one drop of solution of ferric chloride. With the portion known to contain morphine, a blue color appeared *at once*; with the simple extractive matter from the viscera, only a light green color appeared, not changing at all in three minutes; slightly darker in five minutes; after ten minutes one could easily distinguish the samples one from the other, but after two hours both had deposited a similar blue precipitate.

During the process of extraction of the different organs, it was noticed that from them, and particularly from the liver, brain, spleen, intestines, and kidney, a decided odor resembling that of trimethylamine was given off, continuing all the way through.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
June 2, 1894.

FERMENTATION OF GLUCOSE SYRUPS.

BY HORACE E. HORTON.

Received October 23, 1894.

I WOULD like to call attention to the interesting fact that glucose syrup of 41° Bé. is fermentable. The opinion is general that glucose of this gravity is non-fermentable and I am unable to find any published record of such fermentation.

During the summer of 1893 large quantities of the so-called "mixing glucose" sold in southern cities was found to be in a

state of active fermentation. It was thought that the samples were of light gravity, but moisture determinations showed 21.1 per cent., the normal quantity for 41° Bé. syrup. This fermentation was found to exist not alone in the 41° syrup but in samples of 42° Bé. containing 20.19 per cent. moisture.

Cultures of the various liquors in the refinery showed that the ferment was introduced into the goods at some point after the 39° Bé. vacuum pan.

To prevent the finished goods from fermenting the following experiments were made with well-known antiseptic materials.

1.46 pounds of 40° Bé. sodium bisulphite added to each barrel of fifty-two gallons. No effect.

One-half ounce boracic acid and one-quarter ounce benzoic acid to each barrel of fifty-two gallons. No effect.

1.46 pounds of 40° Bé. sodium bisulphite, one-half ounce boracic acid, and one-quarter ounce benzoic acid to each barrel of fifty-two gallons. No effect.

TOPEKA, KANSAS, October, 1894.

ON THE TECHNICAL ANALYSIS OF ASPHALTUM.

BY LAURA A. LINTON.

Received September 21, 1894.

IN the year 1837, J. B. Boussingault published his celebrated memoir on the "Composition of Bitumens." In the researches upon which this memoir was based he had discovered that certain bitumens yielded to one class of solvents a portion of their content and to another class of solvents another portion of their constituent hydrocarbons. He called the first portion "Petrolene" and the second portion, "Asphaltene."¹

In 1827² Le Bel and Muntz went over the same ground and in 1883 Le Bel again went over it, adding a few facts in relation to other bitumens than those previously examined but leaving the two substances, petrolene and asphaltene, practically where he found them.³

In 1837 the conclusions based on chemical research were far less exact than at the present time and Boussingault concluded that the substances, petrolene and asphaltene, were simple sub-

¹ *Annales de Chimie et de Physique*, 64, 141.

² *Bull. Soc. Chim.*, 17, 156. ³ *Ibid*, 50, 359.

stances and also that they were identical from whatever sources they were derived. In this conclusion Le Bel in a measure appears to coincide.

It, however, requires no argument to prove, to any one at all familiar with the subject, that petroleum is nothing but a name that covers a great variety of substances, radically unlike, that exist in different forms of bitumen and are only related, in this instance, as being held in solution by a certain limited number of menstrua and which include the whole list of paraffines and iso-paraffines, the olefines, the benzenes and additive benzenes with many other less abundant and well-known substances.

Ethyl ether and so-called petroleum naphtha, which latter is an indefinite mixture of fluid paraffines and iso-paraffines of high specific gravity, are the solvents used; but no determination has been made as to the influence of proportion in the mixtures of the substances dissolved, or as to the relative solvent powers of the two menstrua upon the different constituents of these mixtures. In fact petroleum is nothing but a name which at present covers a vast expanse of the unknown.

It can be safely said that probability favors the assumption that asphaltene is a little more definite; but no certainty attaches to the identity of asphaltene from different sources or of asphaltene dissolved by different menstrua.

Therefore, in a general way, it may be said that asphaltene is that portion of the different forms of bitumen that is soluble in carbon disulphide, chloroform, benzene and a few other less well-known liquids and is not soluble in the menstrua that dissolve petroleum.

As the bitumens examined by the French chemists, above mentioned, have never assumed commercial importance, the questions relating to petroleum and asphaltene have remained matters of scientific interest only. However, since asphalt paving has become a business involving the expenditure of large sums of money these problems are beginning to assume a wide importance outside the laboratory of the chemist and to demand from technologists very serious consideration. Within recent years large numbers of so-called analyses have been reported, which represent various attempts to determine and set forth the rela-

tive value of many samples and kinds of asphaltum, that may or may not be suitable for the many uses to which asphaltum is applied, but more particularly with reference to street paving. Prominent among the chemists who have been more or less extensively engaged in these analyses of asphalts are Mr. Clifford Richardson, Dr. Henry Leffmann, Dr. Samuel P. Sadtler, and Dr. De Smedt.

A perusal of the numerous published reports of Mr. Richardson reveals the fact that in his tests the solvents used for the extraction of petroleum and asphaltene, were petroleum ether and carbon disulphide, while Drs. Leffmann and Sadtler, in their investigations and tests of asphalts, used alcohol—presumably ethyl-alcohol—carbon disulphide, and ether as shown by the report submitted to the Citizens' Municipal Association and the Trades League of Philadelphia.

Neither of these gentlemen describe any process or method employed in obtaining the results stated. It is hardly consistent with the nature of the reports that they should. Nor has Mr. Richardson, in an article published in the *Journal of Analytical and Applied Chemistry*, in the numbers for December, 1892, and January, 1893, given any detailed description of the process he employed in order to obtain the numerous results of analysis that he there uses.

But little satisfaction can be derived from consulting Allen's encyclopedic work so exhaustive upon every subject relating to technical organic analysis.¹

We find therein the following statements and notes concerning the solvents and methods used in the analysis of asphalts: "For the determination of the *total bituminous matters* in asphalt rock and mixtures containing it, C. T. Kingzett extracts the air-dried sample with freshly distilled Russian oil of turpentine, evaporates (*Analyst* 8, 4) the resultant solution and weighs the residue. The matter insoluble in turpentine is washed with ether, the *calcium* and *magnesium* carbonates dissolved in hydrochloric acid and the washed insoluble *siliceous matter* weighed."

"H. P. Cooper prefers carbon disulphide for dissolving out the bituminous matters from asphaltic mixtures."

¹ *Commercial Organic Analysis*, by Alfred H. Allen, London, 1886, 2, 375, 376, 377.

Allen adds in a note, "The carbon disulphide employed for dissolving the bituminous matter must not contain free sulphur. It may be replaced by chloroform or benzene (coal tar naphtha). If the residue left after extraction be dark colored, foreign organic matters of valueless nature are present. Their proportion may be determined by igniting the weighed residue left after dissolving out the asphaltum, recarbonating it with ammonium carbonate, again gently heating it and reweighing. The loss of weight is the amount of *non-bituminous* organic matter present. In the case of samples leaving a white residue after exhaustion with carbon disulphide, the bituminous matter may be simply and accurately ascertained from the loss on ignition, taking care to recarbonate the lime before weighing."

In another note, page 377, he says: "Five grams of the finely divided sample were digested for one hour with fifty cc. of petroleum spirit (sp. gr. 0.7) and the mixture frequently agitated. The liquid is then boiled for a short time, decanted and the residue boiled with another quantity of twenty-five cc. of petroleum spirit. This treatment is repeated eight or ten times until the exhaustion is complete.

"E. Davies (*Pharm. Jour.*, [3], 14, 394), reports that none of the organic matter in Val de Travers asphalt is insoluble in petroleum spirit."

Now, when we take into consideration the fact that turpentine, carbon disulphide, ether, chloroform, and benzene have been used indiscriminately by chemists in the extraction of asphaltene, the question very naturally arises are the results that have been and that are being obtained by these different methods of analysis strictly comparable—that is, are they convertible terms? Will the same asphalt treated with different solvents show in each case the same percentage composition? If not, then it is evident that asphalt taken from different localities and subjected to dissimilar methods of analysis cannot yield results of any value so far as purposes of comparison are concerned. Then again, if turpentine, carbon disulphide, and chloroform give a different proportion of asphaltene in the same asphalt it is just as evident that asphaltene, instead of being a definite

chemical substance, is a mixture, which mixture would doubtless vary in different asphalts.

It was for the purpose of determining whether petroleum ether (paraffines), California naphtha, and ethyl ether are interchangeable solvents of petrolene and whether turpentine, carbon disulphide and chloroform are interchangeable solvents of asphaltene that the research, the results of which are here given, was undertaken. That a series of such tests, faithfully carried out, should lead to the establishment of a method of analysis applicable to all asphalts and, at the same time, reveal something regarding the real nature of petrolene and asphaltene was inevitable.

The specimens analyzed were furnished me by Prof. S. F. Peckham, Chemist of the Union Oil Company of California, and were as follows:

1. *Crude Trinidad Asphaltum*.—From the Warren-Scharf Asphalt Company, of New York City. This specimen contained little or no water, as, for several months, it had been broken in small pieces, and so had lost the water which this asphaltum generally contains.

2. *Cuban Asphalt*.—A commercial sample obtained in New York City.

3. *Kuban Residuum*.—An artificial asphalt obtained from the distillation of Kuban petroleum from the western extremity of the Caucasus Mountains, Russia.

4. *Egyptian Asphalt*.—An Assyrian asphalt taken from the Dead Sea and imported into Egypt. This specimen was obtained in New York City.

5. *Asphaltic Rock*.—From Val de Travers, Switzerland. This asphalt was a sample of natural rock obtained at the office of Wm. H. Delano, representative of the French Company in New York City.

6. *Seyssel Asphaltic Rock*.—From the well-known locality in eastern France, obtained from the same source as No. 5.

7. *Turrellite*.—From a deposit lately discovered in Uvalde County, Texas, consisting of a mass of sea-shells cemented together by bitumen into a solid rock mass. It occurs in a rock formation said to be of Jurassic age, in which formation the Val de Travers rock also occurs. This specimen was obtained from

the office of the Litho-carbon Company of New York City.

8. *Kentucky Asphaltic Rock*.—Obtained from Marshall Morris, Esq., Louisville, Ky.

9. *An Asphaltic Mineral*.—Resembling Gilsonite; reported as coming from Utah.

10. *California Maltha*.—Taken from a well at Summerland, on the coast, near Santa Barbara.

11. *Asphaltum*.—From mines recently opened near Asphalto, Kern County, California, in the eastern foot hills of the Coast Range Mountains, about thirty miles west of Bakersfield.

12. *Asphaltic Sandstone*.—From San Luis Obispo, California.

13. *Asphaltum*.—Picked up on the beach at San Buena Ventura, California, washed in from the Santa Barbara channel.

14. *Asphaltum*.—From the Ojai ranch, Ventura County, California.

15. *Grahamite*.—A so-called asphaltum taken from a vein in Ritchie County, West Virginia.

16. A portion of a compressed brick made from the asphaltic rock taken from the Seyssel mines. Exhibited at the Columbian Exposition.

17. *Hard Artificial Asphalt*.—An asphaltic residue obtained from the distillation of petroleum obtained near Santa Paula, California. It is known in the refinery of the Union Oil Company, of California, as grade "B."

18. *Soft Artificial Asphalt*.—From the refinery of the Union Oil Company, of California, at Santa Paula. Grade "D."

19. *Asphaltic Pavement*.—Obtained from Franklin Avenue, Buffalo, N. Y. It was laid in 1878, of Trinidad asphalt, wax tailings, and very fine sand. It is remarkable as having been laid for fifteen years with almost no need of repairs.

20. *Asphaltic Pavement*.—From Governor's Island, New York Harbor, laid within the Fort at an unknown date, but so old that it has begun to break up from natural causes. Obtained from J. A. W. Pine, of New York City.

21. *Dubb's Artificial Asphalt*.—A so-called asphaltum obtained in operating the Dubb's patent process for the manufacture of asphaltum by adding sulphur to hot Lima-tar and thereby burn-

ing out the hydrogen. This is an asphalt only in name. The specimen was obtained from J. A. W. Pine, of New York City.

22. *Roofing Pitch*.—Obtained from the Mica-asphalt Company, of New York City.

23. *Pitch*.—Obtained as a residuum in the distillation of Scotch blast-furnace tar. This specimen was obtained from the same source as Nos. 20 and 21.

In making tests to determine the best method to be used in the analysis of asphalts the well-known Trinidad and Cuban asphalts were used and all analyses were made in duplicate. In the case of asphalts rich in bituminous matter about a half gram of the material, finely powdered, was used but in the case of asphalts in which the mineral matter constituted a large proportion the quantity was increased to several grams.

The sample was weighed in an Erlenmeyer flask and digested over night in about fifty cc. of petroleum ether; in the morning the clear solution, containing the dissolved petroleum, was passed through a balanced filter and a fresh portion of petroleum ether added to the contents of the flask. The second digestion was continued for two or three hours when the solution, as before, was filtered off and the process repeated until the whole of the petroleum had been removed. The contents of the flask were then thrown upon the filter and thoroughly washed with petroleum ether. Cold turpentine was then poured upon the filter in successive portions until the filtrate passed through colorless when the assumption was made that all the asphaltene and consequently all the bituminous matter had been removed.

The remaining organic matter, not bituminous, was determined by difference, that is, the residue on the filter, after digestion in turpentine, was washed with ethyl alcohol, dried, and weighed in order to determine the percentage of asphaltene after which the residue was burned in a platinum crucible, the difference in weight representing the organic matter not bituminous.

The contents of the crucible were now purely inorganic and, in the case of most asphalts, the residuum was sand more or less colored with iron.

The analysis of Trinidad asphalt under this treatment gave so low a percentage of asphaltene and so large a proportion of

organic matter not bitumen, that it was clearly evident that *cold* turpentine had not dissolved, and could not dissolve all of the asphaltene.

A second set of experiments was then tried in which cold turpentine and carbon disulphide were used as solvents of asphaltene. The results obtained for samples 1 and 2 were as follows:

| Sample. | Petrolene. | Asphaltene. | Other organic matter. | Mineral matter. | Total. |
|------------|------------|-------------|-----------------------|-----------------|--------|
| No. 1..... | 32.54 | 20.3435 | 12.368 | 34.6775 | 99.929 |
| " 2..... | 25.049 | 54.53 | 2.441 | 17.9215 | 99.945 |

The experiment was now made of somewhat varying the method of treatment for the following reasons: First, because of the difficulty of dissolving out the asphaltene while on the filter by simply allowing the solvent to run through it, and secondly, because, in consequence of the high specific gravity of petroleum ether, a considerable portion of sand or other mineral matter, mixed with asphaltene, always adhered to the flask, thus necessitating a separate determination of this portion. The method now employed for the removal of petrolene and asphaltene was the decantation method, and the solvents used for asphaltene were hot turpentine and chloroform.

The samples were digested over night in petroleum ether; in the morning the solution containing the petrolene was, as far as practicable, removed from the flask and the remainder was evaporated over a steam-bath; after weighing, the residuum containing the asphaltene was digested in hot turpentine over the steam-bath, and finally, the whole contents of the flask were poured upon a balanced filter and treated as in the first experiments.

The percentage composition of Nos. 1, 2, and 17, as determined by the decantation method, was as shown in the following table:

| Sample. | Petrolene. | Asphaltene. | Other organic matter. | Mineral matter. | Total. |
|------------|------------|-------------|-----------------------|-----------------|---------|
| No. 1..... | 31.51 | 22.9865 | 11.4195 | 34.073 | 99.989 |
| " 2..... | 25.055 | 52.245 | 5.758 | 16.918 | 99.962 |
| " 17..... | 64.571 | 21.2545 | 13.706 | 0.3613 | 99.8928 |

In carrying out this method a great many determinations were lost, due to the fact that, in evaporation to dryness over the steam-bath, the contents of the flask were in part bumped out. In consequence, this method was soon abandoned as impractica-

ble, and finally, funnels with stop-cocks were employed, in which the contents of the filter could be digested. Boiling hot instead of cold turpentine was used, and, when necessary, the digestion was continued over night, and all the after washings were made with hot turpentine. Numerous trials showed that carbon disulphide dissolves little more than hot turpentine. The last trace of asphaltene, insoluble in either turpentine or carbon disulphide, was removed by chloroform.

In order to determine the relative solvent power of hot turpentine, carbon disulphide, and chloroform, the following method of qualitative analysis was applied to the twenty-three samples enumerated above. From a half gram to one gram of the material was digested over night in a four-ounce Erlenmeyer flask with about fifty cc. of petroleum ether. Next morning the contents of the flask were poured upon a filter, and the undissolved residue washed with petroleum ether until the filtrate was no longer colored. Boiling spirits of turpentine was then poured upon the filter until it passed through colorless, when carbon disulphide was used in the same manner, followed lastly by chloroform. The action of the successive solvents is shown in the following table :

| Sample.
No. | Hot turpentine. | Carbon disulphide. | Chloroform. |
|----------------|---------------------------|----------------------------------|---------------------------------|
| 1. | Dissolves nearly all. | Dissolves a trace. | Dissolves a perceptible amount. |
| " 2. | Dissolves a large amount. | Dissolves a considerable amount. | Dissolves a perceptible amount. |
| " 3. | Dissolves nearly all. | Dissolves a trace. | Dissolves a trace. |
| " 4. | " " " | " the slightest trace. | " the slightest trace. |
| " 5. | " " " | Dissolves a trace. | Dissolves a perceptible amount. |
| " 6. | " " " | " " | Dissolves a perceptible amount. |
| " 7. | " " " | " the slightest trace. | Dissolves the slightest trace. |
| " 8. | " " " | Dissolves the slightest trace. | Dissolves a trace. |
| " 9. | " nothing. | Dissolves nothing. | " " |
| " 10. | " nearly all. | " a trace. | " a perceptible amount. |
| " 11. | " " " | " " | Dissolves a perceptible amount. |

| Sample. | Hot turpentine. | Carbon disulphide. | Chloroform. |
|---------|---------------------------|----------------------------------|----------------------------------|
| No. 12. | Dissolves nearly all. | Dissolves a trace. | Dissolves a perceptible amount. |
| " 13. | " " " | " " | Dissolves a perceptible amount. |
| " 14. | " " " | " " | Dissolves a perceptible amount. |
| " 15. | " a large amount. | " a considerable amount. | Dissolves a considerable amount. |
| " 16. | Dissolves nearly all. | Dissolves a trace. | Dissolves a perceptible amount. |
| " 17. | " a large amount. | " a considerable amount. | Dissolves a considerable amount. |
| " 18. | Dissolves a large amount. | Dissolves a considerable amount. | Dissolves a considerable amount. |
| " 19. | Dissolves nearly all. | Dissolves a trace. | Dissolves a perceptible amount. |
| " 20. | " " " | " " | Dissolves a perceptible amount. |
| " 21. | " " " | " " | Dissolves a trace. |
| " 22. | " a large amount. | " a considerable amount. | " " |
| " 23. | Dissolves a large amount. | Dissolves a considerable amount. | Dissolves a considerable amount. |

Of the twenty-three asphalts examined, there was not one that did not yield some asphaltene on treatment with chloroform; consequently, it is safe to infer that in the analysis of asphalts, unless final washing be made with chloroform, the per cent. of asphaltene will be too low. There was a marked difference observed in the different asphalts as to the manner in which their constituent asphaltene was dissolved on treatment with hot turpentine. In Nos. 4, 5, 6, and 7, and a few others, the asphaltene dissolved out in a few minutes, while in the case of others, notably No. 15, it was a matter of hours, and even of days, before every trace soluble in turpentine could be removed. No. 9 seems to be an asphaltic freak as it contains no petroleum whatever and is insoluble in both hot turpentine and carbon disulphide, while chloroform and amylic alcohol dissolve but the slightest trace.

It was a difficult matter to determine the relative quantity of asphaltene dissolved by the different menstrua, as the only guide used was the color of the filtrate. This suggests a most

interesting research—the fractional, quantitative determination of asphaltene.

From my experience in the analysis of asphalts, I would advise that a preliminary qualitative analysis be always made of each new variety of asphaltum before any quantitative determinations are attempted, care being taken to observe the behavior of different asphalts with the different solvents. This method of procedure is to be recommended, not only because it would prove an economy of time and reagents used, but also because, in this way, much would be learned concerning the nature of petroleum and asphaltene.

A trial was made with Cuban asphalt to determine the solvent power of petroleum ether (87° Beaumé) as compared with that of California naphtha (74° Beaumé) and ethyl ether with the following results:

| Sample. | Solvent for petroleum. | Per cent. of petroleum. |
|---------|-------------------------|-------------------------|
| No. 2. | Petroleum ether..... | 25.8516 |
| " " | California naphtha..... | 32.444 |
| " " | Ethyl ether..... | 32.5455 |

The high percentage of petroleum when California naphtha or ethyl ether are used indicates that the asphaltene is, in part, dissolved, and consequently, that these menstrua can not be used as solvents of petroleum in the determination of asphalts.

In selecting a method for the quantitative analysis based upon the results of these experiments, it is assumed that, until a strictly scientific method is worked out, the present empirical determination of petroleum and asphaltene will continue in use. The three considerations of economy, speed, and convenience, will together control the selection. So long as the significance of the difference between the 25.8 per cent. dissolved by petroleum ether and the 32.5 per cent. dissolved by ethyl ether is an unknown element in the problem—that is, whether it be seven per cent. of petroleum or of asphaltene that is involved—it is better to use petroleum ether, because it is cheap and easily obtained of a uniform quality. So, too, it is better to use boiling hot turpentine followed by chloroform as solvents of asphaltene, and thus rid ourselves of carbon disulphide altogether.

With these considerations in view the following method of analysis is recommended:

Weigh two suitable portions in four-ounce Erlenmeyer flasks, add fifty cc. of petroleum ether, cover, and allow to stand over night. The following morning decant the liquid upon a balanced filter placed within a three-inch funnel provided with a stop-cock in the neck. Add another portion of petroleum ether to the flask, allowing two or three hours for digestion, and decant the liquid upon the same filter as before; this process is to be continued until the liquid ceases to be colored, then transfer the whole of the bitumen to the filter. Dry the flask in a steam-bath and weigh; any increase in weight of the flask should be subtracted from the amount determined as petrolene. Wash the filter and its contents with petroleum ether, place these with the filter counterpoise in a steam-bath, dry, and weigh; the loss in weight of the bitumen represents the petrolene.

Rinse the flask thoroughly with boiling turpentine and add the liquid to the filter in the closed funnel, pour upon the filter a sufficient quantity of boiling turpentine to wholly submerge it, cover and allow the digestion to continue for several hours or over night. Repeat the digesting and filtering with boiling turpentine until the filtrate becomes colorless. The filter should be much smaller than the funnel. Rinse the flask with chloroform and pour upon the filter, add sufficient chloroform to wholly submerge the filter and allow at least an hour for digestion; wash with chloroform until the filtrate passes through colorless, then dry and weigh; the loss in weight represents the asphaltene. The filter is now to be burned in a platinum crucible and, if the asphaltum be combined with limestone, the residue recarbonated with ammonium carbonate, dried in a steam-bath, and weighed, the loss in weight represents the organic matter not bitumen, or coke, in the case of artificial asphaltic residuum, produced by heat.

There is necessity for washing the flask with the different solvents, not only because the petroleum ether is too light to rinse out all of the mineral matter, but also because some of the asphaltene adheres to the flask. Generally the turpentine removes all of the mineral matter, as well as part of the asphaltene, but if it does not, then after the flask is rinsed with chloroform it must be again dried and weighed and the increase in weight added to

the weight of the mineral matter in the platinum crucible. If water be present the asphalt should be dried in a steam-bath to a constant weight before being digested in petroleum ether. It is possible that some natural asphalts might experience a trifling loss of volatile oils at the temperature of the steam-bath, but in most instances such loss would be too slight to be regarded. With care and patience this method has been found capable of yielding very closely concordant duplicate results at each step.

The following table exhibits the results of a number of quantitative analyses made according to this method.

| Sample. | Water. | Petrolene. | Asphaltene. | Other organic matter. | Mineral matter. | Total. |
|-------------------|--------|------------|-------------|-----------------------|-----------------|---------|
| No. 1..... | 2.029 | 32.4455 | 22.1115 | 8.1215 | 35.2865 | 99.994 |
| " 2..... | 0.3911 | 25.4605 | 54.414 | 2.469 | 17.0305 | 99.7651 |
| " 4..... | | 35.087 | 63.183 | 1.7285 | | 99.9985 |
| Not recarbonated. | | | | | | |
| " 5..... | | 8.518 | 3.924 | 25.791 | 61.764 | 99.997 |
| " 6..... | | 7.486 | 4.316 | | 88.198 | 100. |
| " 7..... | | 8.786 | 3.267 | | 87.947 | 100. |
| " 8..... | | 3.349 | 2.4215 | | 94.228 | 99.9985 |
| " 12..... | 0.335 | 11.323 | 3.81 | 1.124 | 83.407 | 99.999 |
| " 15..... | | 49.959 | 50.041 | | | 100. |
| " 17..... | | 64.571 | 21.2545 | 13.706 | 0.3613 | 99.8928 |
| " 18..... | | 63.498 | 29.966 | 6.095 | | 99.559 |
| " 19..... | | 4.387 | 2.831 | 4.102 | 88.65 | 99.97 |
| " 20..... | 0.434 | 6.666 | 1.87 | 3.697 | 87.33 | 99.997 |
| " 21..... | | 66.788 | 31.932 | 1.278 | | 99.998 |

While this research is in no sense complete—it has in fact but opened up a wide field for further work—yet, sufficient evidence has been obtained to show that petrolene and asphaltene are not substances, but empirical terms that designate mixtures of substances soluble under certain conditions in different menstrua.

It is not unfair to assume that in these empirical mixtures, so long known under the names of petrolene and asphaltene, the lower members of all the different groups of hydrocarbons now known may be found. Again—just as some petroleums, which are varieties of bitumen, consist chiefly of paraffines—notably Pennsylvania petroleum—and some, like Russian petroleum, consist of the additive benzenes, while still others contain mixtures of the two, is it not reasonable to presume that solid bitumens, like liquid bitumens, are equally variable in composition?

If this be the case, then it is equally fair to assume that any solvent taken will not dissolve substances of identical composition from different asphalts.

A review of the results here given suggests the query, have the methods heretofore employed for the technical analysis of asphaltum really been analytical at all? Would not a method and process suggested by the results of the qualitative analyses given in this paper and based on the successive application of different solvents and yielding results similar to those of fractional distillation really become analytical, especially if the separate portions dissolved by the different solvents were subjected to such treatment by oxidizing agents as would enable us by a comparison of the products of oxidation to determine to what groups of hydrocarbons the different substances dissolved respectively belong?

I take pleasure in hereby acknowledging my indebtedness to the courtesy of Hon. Thos. R. Bard, President of the Union Oil Co., of California, for the use of the laboratory of the company while engaged in this research.

MINNEAPOLIS, MINN., Sept. 16, 1894.

ACTION OF METALLIC MAGNESIUM UPON MANGANOUS SALTS.

BY JOS. G. HIBBS AND EDGAR F. SMITH.

Received June 18, 1894.

THE statements relating to the action of metallic magnesium upon solutions of manganous salts are contradictory; thus Manck (Ueber d. Verh. d. Magnesium und Aluminum gegen Salzlösungen, Goettingen, 1862) states that metallic manganese is readily precipitated by magnesium from neutral solutions of manganous nitrate or chloride. Phipson (*Jahresb.*, 1864, 192) corroborates this and remarks that the manganese separates as a regulus. The observations of Roussin (*Jahresb.*, 1866, 170), Comaille (*Comptes Rendus*, 63, 556; *Jahresb.*, 1866, 171), and Kern (*Chem. News*, 33, 236), on the other hand, seem to demonstrate that metallic manganese is not thrown out of manganous salts by metallic magnesium.

We have tried the action of the last metal on manganous salt solutions, both in the presence of alcohol and ether. In using

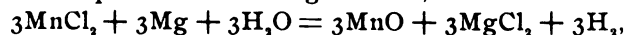
these liquids, our aim was to reduce the liability of oxidation of manganese, if any should appear, to a minimum.

Experiment 1.—In this trial magnesium acted upon aqueous manganous chloride in the presence of alcohol for a period of two hours. At the expiration of this time the liquid was distilled off, and the material remaining was then carefully analyzed. 0.2582 gram substance was used for this purpose. It showed the presence of 0.0284 gram of chlorine, 0.1392 gram of magnesium, and 0.0539 gram of manganese, or a total of 0.2215 gram.

Experiment 2.—In this, both ether and alcohol were added to the solution upon which the magnesium acted. After removal of the liquids the residue was dried in an atmosphere of nitrogen. 0.6530 gram of it showed the presence of 0.0993 gram of chlorine, 0.3059 gram of magnesium, and 0.1865 gram of manganese, or a total of 0.5917 gram. The action of the magnesium in this instance was only continued through one and a half hours.

Experiment 3.—The conditions here were practically the same as those in experiment 2. The substance was dried, as there, in an atmosphere of nitrogen. Upon analyzing 0.7120 gram of the dry residue it revealed the presence of 0.2302 gram of chlorine, 0.2339 gram of magnesium, and 0.1779 gram of manganese.

In these three trials, as in others which were made, the sum total of the constituents of the reaction product, obtained by analysis, is less than the quantity of material taken for analysis, indicating that, in all probability, it is not metallic manganese which is precipitated by magnesium, but rather, a hydrated oxide, as was suggested by Kern, who used a saturated solution of manganous chloride, and allowed metallic magnesium to act upon it for a period of six to eight hours, with this result :



and in the presence of water the manganous oxide passes into the protosesquioxide.

Metallic manganese thrown out by the electric current, oxidizes rapidly on momentary contact with the air, and even if it should come down as metal, through the action of magnesium, it is scarcely probable that, in the finely divided state in which it would be, it could long resist the action of the surrounding water.

NOTE ON THE TEST FOR STRYCHNINE.¹

BY W. P. MASON AND J. W. BOWMAN.

ORGANIC matter having been removed, and the solution containing the purified alkaloid having been evaporated to dryness on the water-bath, the dry residue is taken up with a little concentrated sulphuric acid, one of several oxidizing agents added in solid form, and the well-known strychnine color reaction forthwith appears as usual. Or, in the event of the evaporation having been accomplished in a platinum dish, such dish may be connected with the positive pole of a battery, and, upon touching the negative pole to the acid contents, the strychnine color instantly flashes out. All this being long since known, the following table is offered to indicate the relative degrees of delicacy of the several reagents commonly employed.

In each instance the figures at the top indicate the number of milligrams of strychnine sulphate actually operated upon, *i. e.*, the amount left upon the evaporating dish by the evaporation of the measured quantity of standard solution employed.

| Amount used
in milligrams. | 0.500 | 0.400 | 0.300 | 0.250 | 0.150 |
|--|-------------|-------------|-------------|-------------|-----------|
| K ₂ Mn ₂ O ₈ ... | very strong | very strong | very strong | very strong | strong |
| K ₂ Cr ₂ O ₇ | very strong | very strong | very strong | very strong | strong |
| PbO ₂ | fair | fair | weak | no test | no test |
| K ₆ Fe ₂ (CN) ₁₂ | strong | strong | strong | strong | strong |
| MnO ₂ | strong | strong | strong | strong | strong |
| H ₂ CrO ₄ | very strong | very strong | very strong | strong | strong |
| Battery | strong | fair | no test | no test | no test |
| Amount used
in milligrams. | 0.050 | 0.025 | 0.020 | 0.015 | 0.010 |
| K ₂ Mn ₂ O ₈ ... | strong | strong | weak | very weak | no test |
| K ₂ Cr ₂ O ₇ | fair | weak | very weak | no test | no test |
| PbO ₂ | no test | no test | no test | no test | no test |
| K ₆ Fe ₂ (CN) ₁₂ | fair | fair | weak | very weak | no test |
| MnO ₂ | strong | fair | weak | weak | very weak |
| H ₂ CrO ₄ | weak | no test | no test | no test | no test |
| Battery | no test | no test | no test | no test | no test |

From the foregoing it will be seen that beautiful as Letheby's galvanic test is, it does not compare favorably in point of deli-

¹ Read at the Brooklyn Meeting, August 16, 1894.

cacy with the more common ones using chemical reagents. It certainly fails long before the bitter taste disappears.

From the table it would seem that MnO_2 should be given the first rank, but the slowness of its action is greatly in its disfavor, and the consequent difficulty of getting the color to flow down the side of the dish from the crystal of reagent is an objection. The presence of a little organic matter, also masks its action.

Altogether, we found that $\text{K}_2\text{Mn}_2\text{O}_8$ gave the most satisfactory results. Of course, the color of this reagent is an argument against its use, but if the acid used be of full concentration, and if a blank experiment be run at the same time with acid only in the dish, no trouble need be feared from that source.

RENSSELAER POLYTECHNIC INSTITUTE,
June 4, 1894.

THE DETERMINATION OF MELTING-POINTS AND THE COMPOSITION OF SOME CANDLE MATERIAL.

BY W. E. GARRIGUES.
Received October 15, 1894.

THE so-called melting-point of a fatty substance is obtained in such a variety of ways, and with equally varied results, that the claim of a certain figure for any particular article of commerce is really of little or no value, unless accompanied by a description of the method employed in its determination, which for ordinary trade conditions is hardly feasible.

There is probably no method in common use, even comparatively independent of personal equations and respective laboratory conditions. Those proposed for determining melting-points in capillary tubes etc., besides being open to these objections, necessitate allowing the fat to harden for many hours before applying the test. Wiley's method for butter fat is both tedious and difficult of manipulation and of course useless for free fatty acids.

The solidifying point, after Dalican, is not infrequently reported as the melting-point of stearic acid candles, and would if this were the only material employed, be an easy and fairly good solution of the problem; obviously, however, it is valueless for paraffin-wax and even for many mixtures of the two. The writer believes that any procedure which will quickly give

results on all kinds of candle material, the figures capable of being checked by different manipulators, is a much felt want among chemists engaged in such work.

In American oil refineries the melting-point of paraffin is usually determined by immersing the bulb of the thermometer to two-thirds its length in the molten wax, which is then permitted to cool slowly until the first signs of incipient solidification appear on the surface, disregarding that portion in immediate contact with the sides of the dish. The height of the mercury is then read off.

In some works this is slightly varied by drawing the point of a pin across the surface of the melted wax until a "string" of the latter can be picked up. This is regarded as the melting point.

A modification of Dalican's method, seemingly capable of universal application to substances solid at ordinary temperature was some time ago called to the writer's attention by Mr. Thomas S. Gladding. It consists of observing the temperature at which a fatty substance solidifies while in constant agitation.

The process is conducted by Mr. Gladding in the following manner: Thirty to fifty cc. of the dried sample is placed in a small beaker, the bulb of the thermometer is completely immersed therein and the glass with its contents twirled continuously in one direction until the mercury stops receding or ascending.

At first it falls rapidly and regularly but its subsequent behavior varies with the nature of the substance under examination. With fatty acids there is a rise of from 0.1° to 1° C averaging about 0.3° for commercial stearic acid; here it remains stationary for about one minute. With paraffin-wax no rise results, but the mercury remains stationary about one-half minute and then continues to recede at the rate of 0.1° to 0.2° per minute. The fall prior to reaching this point being much swifter, no difficulty is experienced in noting the exact temperature. With mixtures of stearic acid and paraffin there is great diversity, the observed figures ranging from no rise, to one nearly 4° . The latter representing a mixture of two-thirds stearic to one third wax.

Following is a table showing this melting-point of such mi

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tures in different proportions. The last column gives the action of the mercury at the time of solidification :

| | Stearic. | Paraffin. | Melts at | |
|---------|----------|-----------|----------|-----------|
| 1..... | 100 | 0 | 54.6 | 0.1 rise. |
| 2..... | 100 | 10 | 53.4 | No " |
| 3..... | 100 | 20 | 52.4 | " " |
| 4..... | 100 | 30 | 51.6 | " " |
| 5..... | 100 | 40 | 50.8 | 0.05 " |
| 6..... | 100 | 50 | 50.1 | 0.2 " |
| 7..... | 100 | 60 | 49.2 | 0.6 " |
| 8..... | 100 | 70 | 48.2 | 0.8 " |
| 9..... | 100 | 80 | 47.4 | 2.8 " |
| 10..... | 100 | 90 | 45.6 | 0.6 " |
| 11..... | 100 | 100 | 45.2 | 0.8 " |
| 12..... | 90 | 100 | 45.8 | No " |
| 13..... | 80 | 100 | 46.3 | " " |
| 14..... | 70 | 100 | 46.9 | " " |
| 15..... | 60 | 100 | 47.3 | " " |
| 16..... | 50 | 100 | 47.9 | " " |
| 17..... | 40 | 100 | 48.6 | " " |
| 18..... | 30 | 100 | 48.9 | " " |
| 19..... | 20 | 100 | 49.6 | " " |
| 20..... | 10 | 100 | 50.4 | " " |
| 21..... | 0 | 100 | 50.8 | " " |

To check No. 9, the same paraffin was mixed with another sample of stearic and gave :

| Stearic. | Paraffin. | Melts at | |
|----------|-----------|----------|-----------|
| 100 | 0 | 53.1 | 0.6 rise. |
| 100 | 20 | 50.8 | 0.6 " |
| 100 | 40 | 49.0 | 0.7 " |
| 100 | 60 | 46.5 | 3.6 " |
| 100 | 80 | 45.9 | 3.1 " |

NOTE.—These tables were constructed with a view to practical uses, hence, the proportions, as above, instead of even percentages reckoned on the mixture. In candle factories the predominant material is taken as a basis of calculation. Thus, forty per cent paraffin means 100 parts stearic acid to forty parts wax.

The great advantage claimed for this method is the concordance of its results in different hands. The figures obtained are always the same to 0.1°. The only caution necessary is in cases where apparently no rise of the mercury will take place; the twirling motion should be continued until the mass assumes an unbroken white color and a homogeneous semi-solid consistency. This may take some minutes; then if still no rise occurs the temperature at which there was a pause

is to be noted. A few trials with a mixture like No. 9 will make this clear.

The thing to guard against is being deceived by an action of the mercury similar to say No. 15. For several minutes before the enormous rise in the former, it almost stops, sinking faster than after reaching the true point in the latter. The appearance of the substance under examination is, however, vastly different, being in No. 9, coarse, white flakes floating in a clear molten liquid. On continuing the motion, the mass suddenly blends to a solid white, the temperature rising rapidly to the highest point reached being the melting-point. On paraffin-wax, the refinery test previously mentioned, shows about 0.6° C. higher than Gladding's.

Chemists have for some time been aware that a mixture of fatty acids, subjected to distillation with superheated steam, undergoes some change. It is known that a quantity of liquid hydrocarbons is formed, together with a black pitch; also that there is a slight increment in the melting-point. Alder Wrigley ascribes this latter to the possible formation of isoleic acid or stearolactone. A limited investigation by the writer, carried out at a large candle works, is felt to be a small grain added to a rather barren fund of literature on this subject.

An oft occurring mistake in connection with published analyses of candle material, is the omission of the details of manufacture. For instance, to give the average composition of commercial stearic acid, means absolutely nothing when we consider that one manufacturer employs palm-oil as a source while another uses tallow or bone-fat. A third both saponifies and distills with steam while a fourth uses sulphuric acid or presses the fatty acids directly without distillation. It therefore becomes essential to preface any report of this kind with a brief outline of the several stages through which the fatty substances pass.

The fats under consideration here are exclusively tallow and bone-fat. These are saponified in an autoclave under 150 pounds steam pressure and without the aid of any base. All that is necessary for good color is then at once subjected to pressure at ordinary temperature, followed by a second hydraulic press at steam heat. The solid cake of fatty acids thus obtained

needs only to be freed from dirt before being ready for the candle-molds. The oil expressed hot is permitted to chill, re-pressed cold, and the solid residue again subjected to the hot pressing. This is continuous, the cake from the hot press alone being used in the molding room.

The dark fatty acids, from the autoclave, before receiving the above treatment, are subjected to distillation, in copper, with superheated steam; 16,000 to 18,000 pounds constituting one "run," during which the volume in the still is kept constant by a continuous inflow from the storage tank above.

The distillate is caught in three fractions. The white oil, comprising about four-fifths of the whole is obtained first. This we will call "first run oil;" it is ready for pressing at once. The hydrocarbons that are formed having, in part at least, a higher boiling-point than the fatty acids, accumulate in the still and when these begin to come over in quantity sufficient to color the distillate a decided green, the receptacle is changed. What now comes over we will term "second run oil;" it is returned to the storage tank and redistilled with the next run.

After a time the distillate again changes color becoming darker and more viscid. The operation is then stopped and the contents of the still permitted to cool, subsequently being transferred to a smaller iron still in which a higher heat can be attained. The fraction obtained here we will designate "green oil." There now remains as a residue a black pitch, called "candle tar."

As will be seen later, from its analysis, the practice of returning this green oil to the storage tank, for redistillation with other fatty acids, can not be looked upon in any other light than as an adulteration of the red oils, finally obtained, into which it finds its way.

Going back to the autoclave we find little of interest except perhaps the degree of perfection attained by this mode of saponifying, without any base. Samples removed after ten, twelve, and fourteen hours digestion, showed respectively 1.74, 1.44, 1.06 per cent. glycerol.

NOTE.—The unsaponified fat may be approximately deduced on multiplying these figures by ten.

As might be expected, no change occurred in the constitution of the fat, other than the removal of glycerol. Facilities for trying the effect of higher pressure than 150 pounds were lacking.

Proceeding to the distillation, we find the following changes take place:

| BEFORE DISTILLATION. | | AFTER DISTILLATION. | |
|----------------------|------------------------------------|---------------------|-----------------------|
| Melting-point. | Per cent. oleic acid. ¹ | Melting-point. | Per cent. oleic acid. |
| 41.5 | 43.96 | 44.5 | 35.06 |
| 43.6 | 44.64 | 45.5 | 36.06 |
| 43.9 | 41.67 | 45.0 | 34.00 |

These melting-points are lower than those of the pure fatty acids alone; due in the first column to the presence of neutral glycerides, to the extent of ten to fifteen per cent., and to hydrocarbons from a previous distillation, as before mentioned. Distillation almost eliminates the former, but the hydrocarbons are still there in about the same proportion (*vide infra*).

To determine quantitatively the changes wrought by the high temperature, about 260° C., a run of 16,075 pounds was traced through, and the chemical composition before and after noted, as well as the proportion of the different grades of oil previously named. These figures may be taken as typical, the variations from averages being very small.

The oil had a melting-point of 43.2° C. and contained:

| | Before distillation, per cent. | After distillation, per cent. |
|-----------------------------|--------------------------------|-------------------------------|
| Solid acids..... | 49.52 | 50.47 |
| Oleic acid..... | 42.86 | 33.05 |
| Hydrocarbons (liquid) | 6.94 | 13.14 |
| Glycerol ² | 1.37 | |
| Tar..... | | 2.00 |
| Loss..... | | 1.34 |
| | 100.69 | 100.00 |

The percentage yield of the different grades of oil and its constitution of each was:

¹ NOTE.—All the percentages of oleic acid given in this paper were obtained by calculation from the iodine absorption figure. The melting-points are those described at the beginning of this article.

² NOTE.—One-half the glycerol found is subtracted, together with oleic acid and hydrocarbons, from 100 to determine the solid acids, since tallow glycerides yield approximately ninety-five per cent. fatty acids and ten per cent. glycerol.

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| | | | | |
|-------------------|-------|----------------------------|----------------|---|
| First run oil.... | 80.31 | Containing: Hydrocarbon... | 6.29 per cent. | |
| Melting-point | 44.8 | Fatty acids | 93.71 | " |
| Second run oil.. | 12.13 | Containing: Hydrocarbon... | 35.90 | " |
| | | Fatty acids | 64.10 | " |
| Green oil..... | 4.22 | Containing: Hydrocarbon... | 98.74 | " |
| Tar..... | 2.00 | Fatty acids | 1.26 | " |
| Loss..... | 1.34 | | | |
| | | <hr/> | | |
| | | 100.00 | | |

Making corrections for the hydrocarbons present before distillation and the glycerol, which forms a large part of the 1.34 per cent. loss, we have as a result of distilling 100 parts of pure fatty acids:

| | Before. | After. |
|----------------------------|---------|--------|
| Solid acids..... | 53.61 | 54.63 |
| Oleic acid..... | 46.39 | 35.77 |
| Hydrocarbons (liquid)..... | | 6.71 |
| Tar..... | | 2.15 |
| Loss..... | | 0.74 |
| | | <hr/> |
| | | 100.00 |

It seems reasonably assured, from these figures, that the stearic and palmitic acids distill without change, while the oleic partly splits up into liquid hydrocarbons, tar, and a saturated or non-iodine consuming fatty acid. The nature of this body, though it has not been isolated, will be considered briefly farther on.

From the foregoing facts, it appears to the writer that the present process of manufacture might be advantageously altered by taking the fatty acids directly from the autoclave to the presses—as is done with the light colored stock—and obtaining a press-cake melting at 55°–56°, which latter is then subjected to distillation. By these means the candle stock would not deteriorate in the still as it now does (*vide infra*), and the formation of valueless—and even for most purposes harmful—hydrocarbons would be avoided, giving the red oils a greater worth.

Practical candle makers find that distilled stock invariably yields a press-cake of lower melting-point than that from the autoclave. This is now explained by the formation of the saturated fatty acid from oleic acid, in the still. This body is sufficiently solid to resist being pressed out with the oleic acid, yet

soft enough to lower the melting-point of its associates—stearic and palmitic.

NOTE.—As shown by several writers, the lowering of the melting-point of a mixture of two fatty acids by the addition of a third, does not necessitate the latter having a melting-point below that of the two former.

Apart from the evidence already given its presence is indicated by its low molecular weight, being—probably considerably—under 268, while the mean of stearic and palmitic as occurring in tallow is 271–272. The following tabulated analyses of press-cakes in different stages of completion, illustrate these points.

| AUTOCLAVE STOCK. | | | | STILL STOCK. | | | |
|------------------|------------------------|-----------------------------|--------------------------------|---|-----------------------------|--------------------------------|---|
| | Melting-point,
° C. | Per cent.
oleic
acid. | Total
mean equiva-
lent. | Molecular
weight of
solid
acids. | Per cent.
oleic
acid. | Total
mean equiva-
lent. | Molecular
weight of
solid
acids. |
| 1.... | 51.0 | | | | 16.69 | | |
| 2.... | 51.5 | 21.08 | | | | | |
| 3.... | 53.6 | | | | 7.02 | | |
| 4.... | 53.8 | 11.57 | | | | | |
| 5.... | 54.1 | 9.00 | | | | | |
| 6.... | 54.3 | | | | 6.51 | 269.2 | 268.3 |
| 7.... | 54.4 | 8.40 | | | 5.51 | 269.2 | 268.4 |
| 8.... | 54.5 | | | | 5.96 | 268.4 | 267.5 |
| 9.... | 54.6 | | | | 6.00 | 268.0 | 267.0 |
| 10.... | 54.8 | | | | 4.99 | 268.4 | 267.6 |
| 11.... | 54.9 | 6.60 | 272.0 | 271.2 | 4.16 | 270.0 | 268.4 |
| 12.... | 55.5 | 4.37 | | | | | |
| 13.... | 55.6 | 4.02 | 272.0 | 271.5 | | | |
| 14.... | 56.0 | 3.74 | 272.8 | 272.4 | | | |
| 15.... | 56.1 | 3.96 | 272.0 | 271.5 | | | |
| 16.... | 56.2 | 3.03 | | | | | |

NOTE.—The average content of neutral glycerides was determined to be 3.90 per cent. in samples 11, 13, 14, 15, from the autoclave, which is offset by an average of 0.17 per cent. hydrocarbons in samples 6 to 11, inclusive, from the still. In calculating the mean equivalents, no corrections were made for these in either case. The method of determination was; boiling with an excess of alcoholic potash and back titrating.

To sum up, in conclusion, it appears that when oleic acid is distilled in an atmosphere of steam, the distillate contains, besides unaltered oleic acid, hydrocarbons—liquid, and mainly of high boiling-point—and one or more fatty acids, not isomerides of oleic, having a considerably higher melting-point and lower mean equivalent than the latter, and differing therefrom in not forming addition products with iodine. A black pitch remains as a residue in the still.

SOME RECENT CONTRIBUTIONS TO OUR KNOWLEDGE OF METALLIC REDUCING AGENTS.¹

BY H. F. KELLER.

IN the extraction of metals from their oxygen compounds, carbon is certainly the most important and useful reducing agent. Its great affinity for oxygen is utilized in the manufacture of iron and steel; the commercial production of other useful metals, such as copper, lead, zinc, and tin is accomplished, either directly or indirectly, with its aid; and under its influence even the energetic metals of the alkalis release their powerful grip upon oxygen. Contrasted with this, the use of other substances for the purpose of abstracting oxygen is almost insignificant. Is it surprising, therefore, that carbon is looked upon as the reducing agent *par excellence*, or that the very idea of reduction seems to us inseparably associated with this element?

But the reducing power of a substance depends, in a large measure, upon temperature. It is well known to chemists that, under certain conditions, many metals have affinities which are far more powerful than those of carbon. When we glance over the pages of our chemical text-books, we see described there numerous experiments based upon the superior combining power of iron, aluminum, zinc, magnesium, and the alkali metals. The great Swedish chemist who arranged the elements according to their supposed affinities in an electro-chemical series, was among the first to employ the positive alkali metals for isolating and preparing other elements. His method consisted in decomposing the halogen compounds by means of potassium; and it was subsequently improved by Berzelius' distinguished disciple, Wöhler. With its aid, the latter chemist not only succeeded in reducing for the first time those remarkable metals, aluminum and glucinum, but he also showed that *all* those metals, the oxides of which cannot be reduced by either carbon or hydrogen, may be obtained by the action of potassium upon their halogen compounds.

It must not be supposed, however, that the use of metals as reducing agents is confined to the laboratory and the lecture

¹ First published in the Journal of the Franklin Institute, October, 1894.

table. Practical applications of such reactions may be less conspicuous, but they constitute, nevertheless, the basis of a few important metallurgical processes. The "precipitation of lead from its sulphide ores; the solution of silver by the nascent lead in the blast-furnace; the amalgamation of the same metal in the iron pan; Deville's process of extracting "silver from clay," recently so greatly perfected by Castner and Netto—they are not essentially reductions by means of metals?

In view of the facts mentioned, it may appear strange that comparatively little progress was made for many years in the study of the reducing properties of metals. We can, however, satisfactorily account for this when we consider the great tendency of metals to form alloys; it is difficult, in many cases indeed impossible, to obtain products entirely free from reducing metal, and it is also well known that even a trifling amount of such an impurity may seriously impair the valuable qualities of a metal. Another obstacle has been the high price of those metals, which, by reason of their more powerful affinities, could, with advantage, be substituted for carbon.

Recent improvements in the commercial production of several of these metals have partially removed the latter obstacle. Thanks to the rapid progress of electro-metallurgy, aluminium is now to be had for about half a dollar per pound; sodium, once a chemical curiosity, is manufactured on an enormous scale at a less cost even than aluminum; and magnesium, now successfully extracted from carnallite, is applied to a variety of technical uses.

The radical changes which have taken place in our views of chemical affinity, as a result of the study of thermo-chemical phenomena, and the theory that the properties of the elements are *periodic functions* of their atomic weights, have also largely contributed to awaken interest and activity in the subject of discussion.

The remarkably high heats of formation of its oxide and chloride, as well as the great stability of these compounds, render the action of magnesium upon other oxides and chlorides particularly interesting. Clemens Winkler, of Freiberg, has presented us with a most careful and systematic investigation

the reducing action of this metal upon oxides, while Seubert and Schmidt have communicated a similar exhaustive study of its action upon chlorides.

In giving a brief résumé of the results obtained by these experimenters, I shall adhere to the order adopted by them. It is based upon the periodic system, and has the advantage of showing many interesting relations that might otherwise escape notice.

GROUP I.

Group I embraces a main group consisting of lithium, sodium, potassium, rubidium, and cesium, and a sub-group consisting of copper, silver, and gold.

Owing to the difficulty of obtaining the oxides of the alkali metals in a pure condition, the carbonates were employed. It was found that to insure the best results three atoms of magnesium are required for every molecule of the carbonate, thus: $\text{Na}_2\text{CO}_3 + 3\text{Mg} = 3\text{MgO} + \text{C} + 2\text{Na}$.

The carbon as well as the sodium are deprived of their oxygen. It was found that, with the exception of cesium carbonate, the alkaline carbonates *suffer reduction* to the metallic state when heated with magnesium, but that the intensity of the reaction diminishes as the atomic weight of the metal increases. Lithium, *e. g.*, whose atomic weight is only seven, was reduced with explosive violence, the metal being completely vaporized, while the tube in which the reduction was effected was shattered to pieces; potassium (atomic weight 39), and rubidium (atomic weight 85) on the other hand, were reduced quickly and without notable vaporization.

The reduction may be made in a tube of hard glass closed at one end; it is better observed, however, by conducting it in a current of hydrogen.

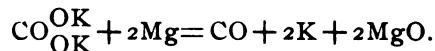
The preparation of potassium affords a most instructive experiment, which may well serve for lecture demonstration.

Into a wide tube of Bohemian glass, a porcelain boat, containing about two grams of the mixture of potassium carbonate, and magnesium is introduced. A current of perfectly dry hydrogen gas is passed through the tube, and the part of the tube surrounding the boat is gradually heated to incipient redness;

the mass darkens, and upon further raising the temperature with the aid of the blast-lamp, the reduced potassium is completely expelled from the boat, exhibiting the deep green color of its vapor, and is deposited in the form of a bright mirror in the cooler part of the tube. At the same time the hydrogen flame shows an intense violet color. The dark residue remaining in the boat consists of magnesia and carbon. Enough potassium will have collected to show its color, luster; that it is sectile, fusible; its action upon water, bromine, etc.

In view of the high price of metallic potassium, the question as to whether the described reaction might not be carried out on the large scale suggested itself. Experiments showed, however, that in the absence of a gas current, the distillation of the metal is very incomplete; and inasmuch as carbon monoxide forms an explosive compound with this metal, illuminating gas could not be substituted; in fact, the explosive carbonyl-potassium was invariably formed when the quantity of magnesium present was insufficient for the *complete* reduction of the carbonate.

This was further proved by experiment. When two atoms only of magnesium were taken, the reaction took place according to the equation:



More promising results were obtained by employing potassium hydroxide instead of potassium carbonate. The danger of forming the explosive body is thus avoided, while the hydrogen gas set free simultaneously with the potassium, insures the complete distillation of the latter:



The reaction is somewhat violent, but may be moderated by adding some inert substance, such as magnesia, or by using the magnesium in the form of lumps or bars.

Winkler says "it does not seem unlikely that the manufacture of potassium could be carried out by means of the same apparatus, and the same operations, which C. Netto has so successfully employed in reducing caustic soda with carbon. Into a retort filled with bars of magnesium, and heated to redness, melted potash would be allowed to flow in a continuous stream, while

the escaping mixture of potassium vapor and hydrogen is being cooled."

Winkler figures the cost of a pound of potassium to be about \$3.75; the metal is now quoted at \$28.

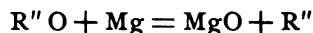
Beketow, who had previously made use of the action of aluminum upon potassium hydroxide, obtained only one-half of the theoretical yield owing to the simultaneous formation of potassium aluminate.

The sub-group, consisting of the heavy metals copper, silver, and gold, exhibited the reverse behavior; the reduction was more energetic the higher the atomic weight of the metal. A very *slight* deflagration accompanied the removal of oxygen from cuprous oxide, while silver oxide was reduced with *explosive violence*. Very curiously aurous oxide was not visibly affected by the magnesium. This is explained, however, by the fact that gold oxide splits up into its constituents considerably below the ignition point of magnesium.

GROUP II.

The main group comprises glucinum, magnesium, calcium, strontium, and barium; and zinc, cadmium, and mercury, constitute the sub-group.

These elements are bivalent, and the action of their oxides upon magnesium is therefore:



In some cases the *hydroxides* were also used.

Glucina was easily reduced by magnesium; the mass became slightly incandescent, but some unaltered oxide was found in the residue.

There was no action observed when a mixture of magnesium and magnesia was heated in hydrogen; the oxide remained in the boat, while the metal sublimed in beautiful crystals. The existence of Beetz's suboxide could not be confirmed.

No visible sign of chemical action occurred when lime and magnesium were heated together. The reduction proved nevertheless to be almost complete.

A slight incandescence attended the reduction of strontia, whilst barium oxide displayed an energetic action upon magnesium. In both cases the decomposition was apparently complete.

None of the alkaline earth metals were found to be volatile at the temperature of reduction.

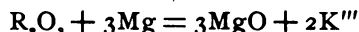
The hydroxides were even more readily acted upon than the oxides; so striking and beautiful, indeed, were the phenomena observed in the cases of calcium hydroxide and strontium hydroxide, that Winkler proposes to utilize them for lecture illustration, and in pyrotechnics.

The reduction of the oxides belonging to the sub-group was very energetic, the resulting metals being vaporized completely. Cadmium oxide develops less energy than either zinc oxide or magnesium oxide.

Both in the main group and the sub-group, the maximum of chemical energy occurs in the second member.

GROUP III.

The main group embraces boron, aluminum, (scandium,) yttrium, lanthanum, and ytterbium, and gallium, indium, and thallium, form the sub-group. Three atoms of magnesium are required to abstract the oxygen from their oxides:

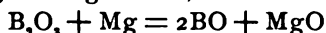


Phipson has observed that boric acid is reduced upon ignition with magnesium. With the aid of magnesium, boron was also obtained by Geuther from the boro-sodium fluoride, and quite recently L. Gattermann has shown that boric acid, as well as borax can be reduced by means of this metal, so as to yield products which are suitable for the preparation of various volatile boron compounds.

Winkler confirmed these observations. He states that the trioxide and the borate of sodium are easily reduced, the latter with much energy and evolution of sodium vapor. But he found that, instead of free boron, the residue contains magnesium boride of variable composition; for, on treatment with hydrochloric acid, boron hydride is given off as a gas. Sometimes a solid residue remains, which is likewise a compound of boron and hydrogen.

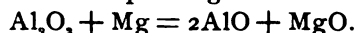
Owing to the acid-forming character of boron, the reduction was never complete; borates, upon which magnesium has no action, are always formed.

An attempt was also made to prepare a boron suboxide by limiting the supply of magnesium, thus:



but no indication of such an oxide was observed.

A dark colored product resulted from heating alumina with magnesium. The reaction appeared to be quite energetic; the mass exhibited a vivid glow and increased largely in volume. In addition to finely divided aluminum, a new oxide, AlO , and magnesium spinel had been formed. This monoxide could not be obtained in a pure condition, but its existence was proved beyond doubt. It is best prepared by heating in a current of hydrogen, a mixture corresponding to



This oxide is a brownish-black, voluminous powder, is pyrophoric, and liberates hydrogen slowly from water; it precipitates cuprous oxide from copper sulphate solution, and is exceedingly susceptible to oxidation.

Winkler suggests that the blue color of sapphire, and possibly also that of ultramarine, may be due to a small proportion of this monoxide.

Of the rare earths of group III, only yttria and lanthana were subjected to the action of magnesium. The energy of the reduction appeared to increase with the atomic weights.

Upon the oxides of the sub-group, magnesium reacts with great violence; the intensity of reduction has its maximum in In_2O_3 .

The behavior of Tl_2O_3 towards magnesium, appears to be an exception. Before the temperature of reduction is reached, this oxide splits up into Tl_2O and O_2 , and the thallos oxide so formed is then only partially reduced. Thallium carbonate, however, is deprived of its oxygen completely and with explosive violence.

GROUP IV.

The most interesting results, perhaps, were obtained in the fourth natural group of elements.

The known properties of carbon, silicon, titanium, zirconium, cerium, and thorium, assign them positions in the main group, while germanium, tin, and lead, constitute the sub-group.

In addition to their acid-forming dioxides, the majority of the elements are capable of giving monoxides. It was therefore deemed desirable to attempt not only the complete reduction of the higher oxides, but also a *partial* removal of the oxygen in a view to procure the lower oxides.

The statements of different experimenters concerning the action of carbon dioxide upon magnesium are somewhat conflicting.

That a ribbon of the metal will burn in an atmosphere of carbon dioxide was first observed by Kessler, but neither he nor other chemists who repeated and modified his experiments explained satisfactorily the nature of the reaction.

Winkler shows, in the first place, that magnesium, when *gradually* heated in a current of carbon dioxide, does not take fire but is slowly converted at its surface into a carbide, carbon monoxide being formed at the same time. Upon increasing the heat to a full redness, the metal was inflamed and continued to burn with a dazzling light. The products of this combustion are magnesia and carbon.

When the magnesium is employed in the form of powder, the reactions take place even more readily. At a temperature considerably below a red heat carbon monoxide appears, and its quantity is greatly increased when low redness is reached. The metal burns with great brilliancy at a full red heat, and when the current of carbon dioxide is very rapid, its reduction is complete.

It has already been mentioned that a separation of carbon was observed when magnesium acted upon carbonates; also carbon monoxide was formed when an excess of the carbonate was present. Further experiments were made with calcium carbonate. A mixture of this substance with magnesium: $\text{CaCO}_3 + 3\text{Mg} = \text{Ca} + \text{C} + 3\text{MgO}$, heated in a current of hydrogen detonated violently. The examination of the debris revealed the presence of a carbide of magnesium. No metallic calcium was observed in the residue when only two atoms of magnesium were used for each molecule of the carbonate.

According to Kessler, burning magnesium is extinguished by carbon monoxide, while Parkinson asserts that at a red heat

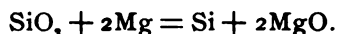
metal burns vividly in this gas. Both observations were found to be correct. A spiral of magnesium wire ignited in the air, ceased to burn while introduced into a jar of carbon monoxide, but when strongly heated in a current of the gas the magnesium emitted light, and a gray coating of a carbide appeared on its surface.

Numerous experiments to determine the exact composition of this carbide were made, but without yielding a definite result.

Silicon exhibits a pronounced tendency to combine with magnesium. Silicon-magnesium was first observed by Wöhler, in 1858. •

The reduction of silica by metallic magnesium was observed in 1864, by Phipson, and Parkinson showed in 1867 that silicon-magnesium, as well as a magnesium silicate, are formed at the same time. A few years ago L. Gattermann published an interesting paper, in which he showed how very easily silicon dioxide is reduced by magnesium. He states that either silicon or silicon-magnesium can be obtained by varying the proportion of magnesium; and he applies the reaction to the preparation of volatile compounds of silicon, such as the chloride, bromide, iodide, silicoformic acid, silico-chloroform, etc.

Gattermann and Winkler agree that an energetic reaction occurs upon heating a mixture of one molecule of silica and two atoms of magnesium.



By adding magnesia to the mixture, the heat of the reaction was moderated, but it was then found that much silicon-magnesium was contained in the product. If the reaction be effected at low temperature and in the presence of an excess of magnesium, silicon-magnesium is always formed, while at a high heat or in presence of magnesium, only amorphous silicon results.

A silicon monoxide could not be obtained by the reduction of silica, either by magnesium or silicon.

Many silicates are reduced quite as easily as the dioxide; in some cases the metallic base is likewise reduced, *e. g.*, potash glass.

None of the oxides studied presented greater difficulties than

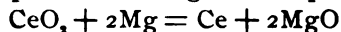
titanium dioxide. The results may thus be summed up: Titanium dioxide was not reduced to the metallic state; a mixture of monoxide and a titanium spinel were the products of the reaction. Other intermediate oxides were sometimes formed. When the residue was treated with hydrochloric acid, HTi_2O_4 was formed, which, upon heating, gave TiO_2 and hydrogen. Neither titanium-magnesium, nor a titanium hydride, was observed.

The reduction of zirconia was effected by heating it with magnesium to a high temperature. A monoxide could not be identified with certainty; and ZrMg_2 does not appear capable of existing.

According to the amount of magnesium employed either cerium or Ce_2O_3 were obtained from cerium dioxide. An intermediate monoxide was not formed. The reduction begins at a moderate red heat and is accompanied by a vivid glow. A considerable proportion of the magnesium is volatilized. In the nascent state, cerium was found to absorb hydrogen in large quantities.

The formation of a metallic hydride at a bright red heat is a most remarkable observation. It is clearly proved to be correct by the following experiment.

A mixture is prepared according to the equation:



Twenty grams of this mixture are placed in a combustion tube through which a current of dry hydrogen is passed, while a gentle heat is applied to expel any moisture. The further end of the tube is then closed with a strong clip. Hydrogen is allowed to enter the other end and the heat quickly raised to bright redness; a rapid current of hydrogen is seen to pass through the wash-bottles into the tube.

The hydride is of a brownish-red color. It is without action on water at ordinary temperatures, but sets free hydrogen upon heating. Hydrochloric acid dissolves it to CeCl_3 , with evolution of hydrogen. It was found impossible to completely remove magnesia from the product. The hydride is very inflammable, and detonates with potassium chlorate, potassium nitrate, etc.

The analytical results obtained point to the formula CeH_2 .

After the existence of a cerium hydride had thus been established, the thought suggested itself that the other elements of Group IV might possibly be capable of forming similar compounds. Only carbon and silicon were known to form hydrides, but these elements could not be made to unite with hydrogen when their oxides were reduced by magnesium. Since titanium could not be reduced to the metal, it is not strange that all efforts to form a hydride gave negative results; zirconium and thorium did absorb hydrogen and yielded hydrides similar to CeH_3 . The same was observed with lanthanum and this led Winkler to believe that this element belongs to the cerium group; but he showed subsequently that yttrium and other trivalent elements, and even the divalent barium, strontium, and calcium can unite with hydrogen.

These hydrides represent a new class of metallic compounds, in which only half the usual valence of the metals is satisfied.

The action of magnesium upon chlorides has been made the subject of an elaborate research by Seubert and Schmidt.

I must content myself with a very brief statement of some of the main results obtained by these chemists.

Both the anhydrous bodies and the aqueous solutions of the chlorides were subjected to the action of magnesium.

In the former case the substance, either mixed with magnesium powder, or conducted over it in the form of vapor, was heated to a high temperature. It was found that all chlorides could thus be reduced to the metallic state, but the reduction was incomplete in the groups of the metals of the alkalies and the metals of the alkaline earths.

In *neutral* aqueous solutions, all the metallic chlorides, save those of the alkalies and those of the alkaline earths, gave up their chlorine to the magnesium. In some cases the metals were deposited in the metallic state, (silver, gold, thallium, lead, arsenic, antimony), but in most cases, hydroxides were precipitated. These hydroxides always represent the lowest state of oxidation. CuCl_2 , *e.g.*, is changed into Cu_2O ; chromium, aluminum, iron, manganese, cobalt and nickel, all yielded hydroxides.

It would seem that the tendency to form such hydroxides is

peculiar to the positive metals, and especially to those forming basic salts. Seubert and Schmidt believed this to be due to a dissociation of the chlorides into hydroxides and hydrochloric acid. They suppose, for instance, that an aqueous solution of AlCl_3 contains $\text{Al}(\text{OH})_3$, 3HCl . This view is rendered quite probable by the fact that solutions of copper, nickel, cobalt, and chromium exhibit the color of their *hydrated* salts.

Of other metals whose oxides possess a high heat of formation, aluminum has found some application in the reduction of oxides. Beketow has employed it with success to prepare some of the metals of the alkalis; and the experiments of Greene and Wahl of reducing manganese oxides by means of metallic aluminum are still fresh in our memory.

I am convinced that a continued study of the relative affinities of the metals for oxygen and other negative elements, will lead to important applications in metallurgy, and give new and valuable methods to synthetic and analytical chemistry.

OBSERVATIONS ON AMERICAN OIL OF TURPENTINE.

By J. H. LONG.

Received October 24, 1894.

IN the February, 1893, number of the *Journal of Analytical and Applied Chemistry* I called attention to certain peculiarities of our American turpentine-oil as distilled from the crude turpentine produced in the southern states.

It is well known that the chief difference between the so-called French and American turpentines is found in their behavior toward polarized light, the French oil being laevo-rotatory, while that produced here has always been described as dextro-rotatory.

In the course of the examination of a large number of samples distilled in the laboratory from fresh crude turpentine sent me directly, I found that some disclosed a very low rotation, and a few were even laevo-rotatory. Through the courtesy of Mr. E. B. Martin, of Louisville, I was supplied with crude "gum" collected in small amounts from single trees, and from the tests of these samples it appeared that the laevo-rotation was

found only in the product from the so-called spruce trees, sparingly represented in the lower turpentine-producing region. As this spruce pine (*P. glabra*) is not considered important from the standpoint of the industry I found difficulty in securing material enough for satisfactory investigation. However, in April of this year six samples of the dip, or crude liquid exudation, collected near Mobile, from as many different trees, were sent me and from these I distilled the oils used in the tests below.

In odor, color, specific gravity, and boiling-point these oils showed no unusual features, the average specific gravity at $\frac{20^{\circ}}{4^{\circ}}$ being 0.862. When examined by the polarimeter, using the 200 mm. tube, I found the "observed angle of rotation," α , as follows:

| | | | |
|-------|--------------|-------|-------------------|
| No. 1 | $\alpha_D =$ | | -64.750° |
| " 2 | " | | -69.075° |
| " 3 | " | | -64.541° |
| " 4 | " | | -63.100° |
| " 5 | " | | -63.333° |
| " 6 | " | | -70.333° |

The laevo-rotation is in all cases very marked, the specific rotation in the last amounting to

$$[\alpha]_D = \dots\dots\dots -40.79^{\circ}$$

It is also interesting to note that the results are close for the six samples, but as the trees yielding them grew in the same orchard, and, therefore, under practically the same conditions, and as the samples were taken at nearly the same time, this agreement should not be unexpected. It may be recalled that the laevo-rotation of the French oil has usually been found much more uniform than the rotation of the American oil.

These observations seem to show the probable correctness of my former suggestion; *viz.*, that the negative rotation sometimes found in American oil may be due to the presence of products from spruce trees. This appears all the more probable when it is remembered that in numerous oils examined, known to be free from spruce, a marked positive rotation was always noted, while a low positive rotation was found only in those oils distilled in parts of the country where the spruce is occasionally found.

In the further study of these oils I mixed distillates 1 and 3 above and redistilled fractionally. The fractions were polarized as before with the following results:

| Temperature. | | α_D in 200 mm. tube. |
|--------------|----------------|-----------------------------|
| 156. | to 156.7 | —69.133° |
| 156.7 | " 157.2 | —67.683° |
| 157.2 | " 157.6 | —65.930° |
| 157.6 | " 159.4 | —63.200° |
| 159.4 | " 162.7 | —57.883° |

A mixture of 2 and 6 gave:

| Temperature. | | α_D in 200 mm. tube. |
|--------------|----------------|-----------------------------|
| 156. | to 156.2 | —73.350° |
| 156.2 | " 156.7 | —72.416° |
| 156.7 | " 157.2 | —71.066° |
| 157.2 | " 158.7 | —68.865° |
| 158.7 | " 162.7 | —65.160° |

These results confirm those obtained from other oils, showing that the absolute amount of rotation is decreased in the higher fractions.

It was stated by Berthelot (J. B., 1853, p. 522) that the dextro-rotatory American oil when heated in sealed tubes to above 250° is transformed into a substance with higher boiling-point and negative rotation. To test this behavior in the present case I heated a portion of the first fraction from 1 and 2 to a temperature of 280° during two hours in a sealed glass-tube. On cooling it was polarized without redistillation, and showed in the 200 mm. tube

$$\alpha_D = \dots\dots\dots -15.33^\circ.$$

The product was then sealed and heated again to 300° through several hours. On cooling, it was found to be yellowish and somewhat viscid; on distillation the liquid was found to have a much higher boiling-point than the original turpentine, but little passing over below 170°.

Three-fourths of the product distilled between this point and 250°, and this portion polarized gave in the same tube

$$\alpha_D = \dots\dots\dots -19.560^\circ.$$

A fraction of the distilled liquid collected from 175°–180° was strongly laevo-rotatory also.

The residue was very dark and became thick and resinous on

exposure to air. The distilled liquid had a marked odor of oil of lemons and this with its rotation suggest that it must be identical with the product described by Berthelot as iso-terebenthene, which may be obtained also from the laevo-rotatory French oil. While the ordinary product of long heating of turpentine-oil seems to be inactive dipentene we have here a very stable active product which is probably mainly laevo-limonene.

CHICAGO, October 22, 1894.

IRIDIN, THE GLUCOSIDE OF THE IRIS ROOT.

BY G. DE LAIRE AND FERD. TIEMANN.

[TRANSLATED AND ABRIDGED BY S. S. EMERY.]

(Continued from Page 411 of Volume XV.)

Iretol.—Iretol, the third decomposition product of irigenin, may be separated from the alkaline solution of the three by supersaturating with dilute sulphuric acid (1 : 2), neutralizing with potassium carbonate, and, after filtering from the separated potassium sulphate, shaking ten to twelve times with ether, which dissolves only the iretol. The ether can not be completely distilled from this extract, as the crude iretol forms condensation products which are insoluble in water and ether; hence the last portion of the ether must be allowed to evaporate in the air. The iretol thus obtained is a crystalline mass, easily soluble in water, alcohol, ether, and acetic ether. By fractional precipitation by chloroform from the acetic ether solution it is obtained as white needles, melting at 186°.

Its molecular weight was found to be :

| 1. | 2. | |
|---|---|------------------------------------|
| By the lowering of
the freezing-point
of a glacial acetic
acid solution.
(Raoult's method.) | By the raising
of the boiling-
point of an
alcoholic solution. | Calculated
for
$C_7H_8O_4$. |
| 181.2 | 159 | 156 |

It contains one methoxyl group, as shown by the following determinations:

ANALYSIS.

| | Per cent. (OCH ₃). |
|---|--------------------------------|
| Calculated for $C_6H_5O_3(OCH_3)$ | 19.87 |
| Found..... | 17.26—19.22 |

Tribenzoyliretol, $C_{28}H_{20}O_7 (CO.C_6H_5)_3$. — Tribenzoyliretol obtained by treating an absolute alcohol solution of one mole iretol and three molecules of sodium ethylate with a slight excess of benzoyl chloride and letting stand several days in the dark. It is separated by removing the alcohol by steam, extracting with ether, and, after shaking with dilute soda solution, drying, when it is obtained as an oily substance, which soon after several weeks to a transparent resin, easily soluble in alcohol, ether, acetic ether, benzene and chloroform, but insoluble in water and ligroin.

ANALYSIS.

| | Per cent. C. | Per cent. H. |
|--|--------------|--------------|
| Calculated for $C_{28}H_{20}O_7$ | 71.79 | 4.2 |
| Found..... | 71.03 | 4.6 |

From the foregoing, it is evident that iretol contains two methoxyl and three hydroxyl groups, and that its empirical formula is $C_6H_5(OCH_3)_2(OH)_3$, according to which iretol appears to be the monomethyl ether of a tetroxybenzene. The correctness of this view is established by the conversion of iretol into phloroglucinol.

This is accomplished by treating the cold dilute (1 : 10) alcoholic solution with sodium amalgam, and, after destroying the excess of amalgam by heating on the water-bath, adding an excess of sulphuric acid and then distilling. The distillate consists of very dilute methyl alcohol with traces of acetaldehyde. The ether extraction of the residue, on evaporating, gave phloroglucinol, melting at 208° , its identity being established by the following:

ANALYSIS.

| | Per cent. water of crystallization | |
|--|------------------------------------|--|
| Calculated for $C_6H_6O_3 \cdot 2H_2O$ | 22.22 | |
| Found..... | 22.38, 22.6 | |

| | Per cent. C. | Per cent. H. | |
|----------------------------------|--------------|--------------|-------------------------------------|
| Calculated for $C_6H_6O_3$ | 56.98 | 4.76 | } In the analysis of phloroglucinol |
| Found..... | 59.94, 56.71 | 4.64, 4.70 | |

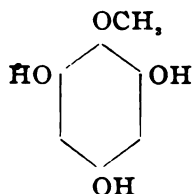
| | Molecules of water |
|--|--------------------|
| Calculated | 1 |
| Found (raising of boiling-point of alcoholic solution).... | 1 |

The triacetyl derivative formed from the phloroglucinol melted at 106° (104° – 106° according to Hlasiwetz¹ and Herzig²). Finally, we prepared tribenzoylphloroglucinol $C_6H_3(OCOC_6H_5)_3$, crystallizing from alcohol and melting at 172° .

ANALYSIS.

| | Per cent. C. | Per cent. H. |
|--|--------------|--------------|
| Calculated for $C_{27}H_{18}O_6$ | 73.97 | 4.11 |
| Found..... | 73.40 | 4.10 |

The phloroglucinol is formed from the iretol according to the equation $C_6H_6O_4 + 2H = C_6H_4O_3 + CH_2OH$, from which it is evident that iretol is a methoxyphloroglucinol, having the constitutional formula



Properties and Reactions of Iretol.—Melts at 186° ; easily soluble in water.

(a) *In Aqueous Solution.*—Violet color, changing to brownish red, with ferric chloride.

Red precipitate of benzeneazoiritol with anilin nitrate, sodium nitrite, and a few drops of strong acid.

(b) *In Alcoholic Solution.*—A white, crystalline condensation product with a solution of benzaldehyde in six times its volume of concentrated hydrochloric acid. Substitution of vanillin for benzaldehyde gives violet-colored solution before precipitation.

The last three tests are characteristic, although also given by resorcinol and phloroglucinol.

(c) *With Bromine.*—In ethereal solution, gives bromine substitution products.

In ethereal solution in the presence of water gives hexabromacetone, $Br_3C.CO.CBr_3$.

¹ *Liebig's Annalen*, 119, 201.

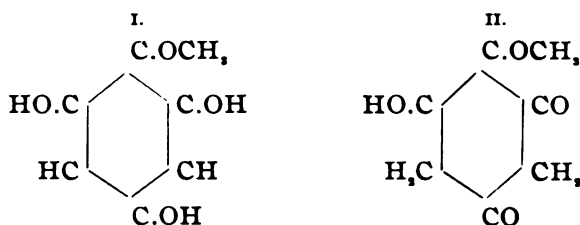
² *Wiener Monatshefte für Chemie*, 6, 888.

Bromine in caustic alkali, instead of free, gives bromoform, the hexabromacetone first formed being readily decomposed by the alkali into carbon dioxide and bromoform.

Sodium nitrite, with acetic acid in slight excess, converts it into the sodium salt of dinitrosoiretol, $C_6H_3NaN_2O_5 \cdot 2H_2O$, separating in red crystals.

Tetroxybenzene 1.2.3.5.—The methyl in the methoxyl group of iretol can be easily replaced by hydrogen, by heating with dilute hydrochloric acid in a closed tube. Monochlormethane is given off. After removing the hydrochloric acid with lead and silver carbonate, and the water by evaporation in a partial vacuum, the tetroxybenzene was obtained as an amorphous substance, soluble in water, alcohol, ether, acetic ether, but insoluble in benzene, chloroform, and ligroin.

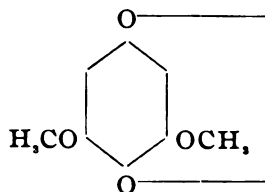
Isomerism of Iretol.—The properties and reactions of iretol, and also the difficulty in obtaining pure the corresponding tetroxybenzene, are explained by its isomerism, its two forms being

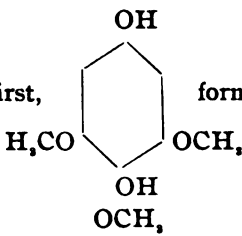


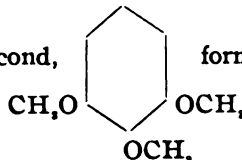
Form II undergoes hydrolysis on treating with alkali, acetone, and acetic acid being found.

This isomerism is substantiated by the following :

Methyl Derivatives of Iretol.—Tetroxybenzene yields a di- and tetra-methyl ether, prepared from the dimethoxyquinol

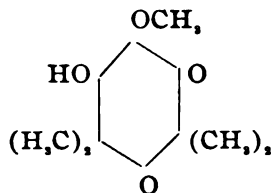


the first,  formed by reduction of the quinol, and the

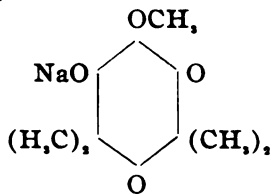
second,  formed by methylating the dimethyl product.

We have not succeeded in preparing this last from iretol.

Tetramethyliretol



is prepared by treating the methyl alcohol solution of iretol (five grams) in an atmosphere of hydrogen, with sodium (three grams) dissolved in methyl alcohol, and with iodomethane (twenty grams). The methylation is induced by shaking the flask, and is accompanied by a rise of temperature. The sodium salt of tetramethyliretol is separated by evaporating and precipitating with concentrated caustic soda. The yield is about one-third of the theoretical, the remainder of the iretol being converted into oily methyl derivatives. The salt crystallizes in long white needles, with three molecules of water, and suffers efflorescence, at ordinary temperatures, in a partial vacuum. Its constitutional formula is



| ANALYSIS. | | | | | |
|--|-----------------|-----------------|------------------|--------------------------------|---------------------------------|
| | Per cent.
C. | Per cent.
H. | Per cent.
Na. | Per cent.
H ₂ O. | Per cent.
OCH ₃ . |
| Calculated for $C_{11}H_{15}NaO_4 \cdot 3H_2O$
($=C_{11}H_{21}NaO_7$).. | 45.83 | 7.29 | 7.98 | 18.75 | 10.76 |
| Found | 45.57, 45.50 | 6.94, 6.99 | 7.76, 7.75 | 18.82, 18.20 | 10.74 |
| In the anhydrous salt: | | | | | |
| Calculated for $C_{11}H_{15}NaO_4$ | 56.41 | 6.41 | 9.83 | | |
| Found | 56.55, 56.04 | 7.17, 7.18 | 9.70 | | |

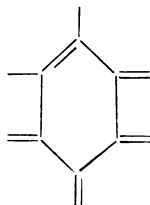
Sulphuric acid liberates free tetramethyliretol, insoluble in ligroin, but soluble in hot water, alcohol, ether, acetic ether, benzene, and chloroform. It crystallizes in glistening white needles, with one molecule of water, melting at 97°; effloresces in a partial vacuum, the anhydrous substance melting at 104°.

| ANALYSIS. | | | |
|--|-----------------|-----------------|--------------------------------|
| | Per cent.
C. | Per cent.
H. | Per cent.
H ₂ O. |
| Calculated for $C_{11}H_{18}O_4 \cdot H_2O$, ($=C_{11}H_{20}O_5$) | 57.39 | 7.83 | 7.83 |
| Found | 56.98 | 7.86 | 8.06 |
| In the anhydrous substance: | | | |
| Calculated for $C_{11}H_{18}O_4$ | 62.27 | 7.55 | |
| Found | 62.41 | 7.51 | |

Benzoyltetramethyliretol, $C_{11}H_{18}(COC_6H_5)_4O_4$, formed by the action of benzoylchloride on the sodium salt of tetramethyliretol in alcoholic solution, crystallizes therefrom in white tablets, melting at 84°.

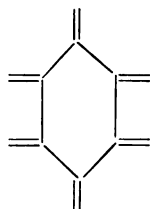
From the constitutional formula of tetramethyliretol (page 851), it is evident that by oxidation it breaks up into dimethylmalonic acid, isobutyric acid, and formic acid. By fusion with caustic potash, these products were actually obtained.

Dihydrotetramethyliretol.—Tetramethyliretol is a derivative of tetrahydrobenzene.



On treating with sodium amalgam, at ordinary temperature,

it takes up two atoms of hydrogen, apparently passing into the hexahydrobenzene form

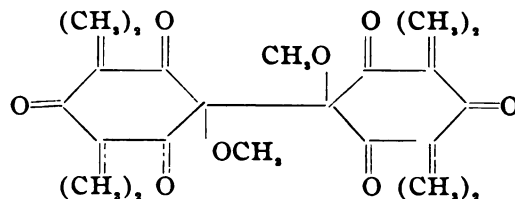


and this view is substantiated by the conversion of iretol into phloroglucinol. After destroying the excess of amalgam by heating on a water-bath, the sodium salt of dihydrotetramethyliretol may be crystallized out, or the free dihydrotetramethyliretol may be obtained by acidifying before crystallizing, when it forms transparent, rhombohedral crystals, containing one molecule of water, which is slowly given off on standing in a partial vacuum. The crystallized substance melts at 107° , the anhydrous at 139° . It is easily soluble in water, alcohol, ether and chloroform, and is precipitated from the latter by ligroin. It is not attacked by bromine nor permanganate, and, in general, does not differ widely from the tetramethyliretol.

ANALYSIS.

| | Per cent.
C. | Per cent.
H. |
|---|-----------------|-----------------|
| Calculated for $C_{11}H_{18}O_4 \cdot H_2O$ | 56.90 | 8.62 |
| Found..... | 56.90 | 8.67 |
| In the anhydrous substance: | | |
| Calculated for $C_{11}H_{18}O_4$ | 61.68 | 8.41 |
| Found | 61.71 | 8.72 |

Dehydrotetramethyliretol, $C_{22}H_{30}O_8$.—



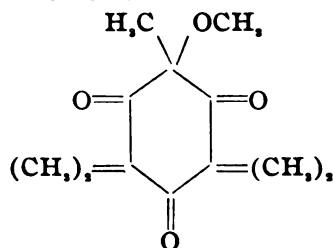
This is formed by the action of ferric chloride on the aqueous solution of sodium tetramethyliretol, two molecules, of which unite, each losing one atom of hydrogen. The precipitation

is attended with a change of color of the solution into deep violet, passing into olive-brown, and finally clear green. It forms white needles, melting at 133° , easily soluble in alcohol, ether, benzene, and chloroform, but insoluble in water. It is very stable, having, in general, the properties of a saturated compound.

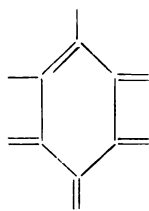
ANALYSIS.

| | Per cent.
C. | Per cent.
H. | Molecular
weight. |
|--|-----------------|-----------------|----------------------|
| Calculated for $C_{22}H_{30}O_8$ | 62.64 | 7.11 | 422 |
| Found | 62.49 | 7.14 | 367 |

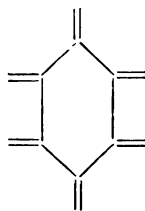
Pentamethyliretol, $C_{11}H_{16}O_4$.—



This is formed by further methylation of the sodium tetramethyliretol by means of methyl iodide. According to this, it is a derivative of tetrahydrobenzene,



and not of hexahydrobenzene.



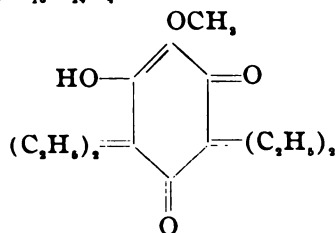
As it has, in general, the properties of a saturated compound, it was thought that rearrangement of the atoms in the molecule of the tetramethyliretol must have taken place in the above process, and this is proved by the methoxyl determination, which shows the presence of but one methoxyl group.

ANALYSIS.

| | Per cent.
C. | Per cent.
H. | Per cent.
OCH ₃ . | Molecular
weight. |
|--|-----------------|-----------------|---------------------------------|----------------------|
| Calculated for $C_{11}H_{16}(OCH_3)O_3$ | 63.72 | 7.97 | 13.72 | 226 |
| Found | 63.62 | 7.98 | 13.63 | 190 |

It crystallizes from a methyl alcohol solution in long white needles, melting at 62° , boiling at 240° , and slowly subliming at ordinary temperatures.

Tetraethyliretol, $C_{14}H_{21}O_5$.—



This was prepared similarly to the corresponding methyl compound. That its constitutional formula is analogous to the latter is shown by the methoxyl determination in the following

ANALYSIS.

| | Per cent.
C. | Per cent.
H. | Per cent.
OCH ₃ . |
|---|-----------------|-----------------|---------------------------------|
| Calculated for $C_{14}H_{21}(OCH_3)_3O_3$ | 67.16 | 8.95 | 11.57 |
| Found | 67.21 | 9.19 | 13.81 |

Its sodium salt being somewhat soluble in caustic soda, it is difficult to isolate from the other products of the reaction, but it may be accomplished by first removing them with ether, when it may be crystallized from the chloroform and acetic ether extraction of the residue by precipitating with ligroin. It forms white, anhydrous prisms, melting at 168° – 169° .

Analogous to the trimethylether of phloroglucinol,



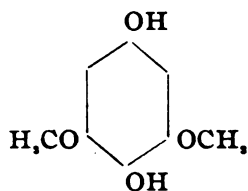
(prepared by saturating the methyl alcohol solution of phloroglucinol with hydrochloric acid gas, and then further methylating the dimethyl product thus formed by using methyl iodide in alkaline solution), we have attempted to prepare the trimethylether of iretol, the tetramethylether of asymmetrical tetroxybenzene, but as yet, without success.

Monomethyliretol, $C_6H_3(OCH_3)_2(OH)_1$.—This is the dimethylether of asymmetrical tetroxybenzene. It is formed by the action of hydrochloric acid gas on the methyl alcohol solution of iretol at 0° . When freshly prepared it is of oily appearance but slowly solidifies to a crystalline mass. When crystallized from boiling benzene it forms white tablets, melting at 87° , easily soluble in

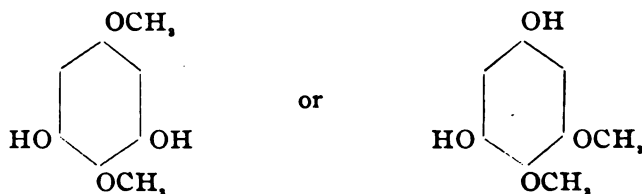
water, alcohol, and ether, but less soluble in benzene and chloroform.

It may be further methylated by the action of methyl iodide on its sodium salt, but instead of obtaining thus a normal asymmetrical tetroxybenzene ether, polymethyl derivatives of methyliretol result, since the methylation takes place in the benzene ring.

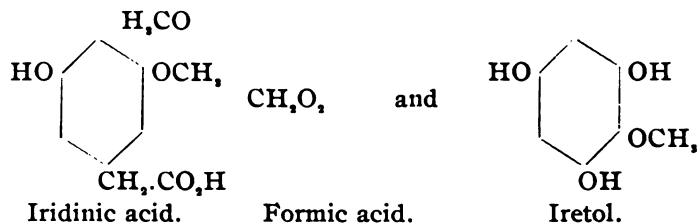
The dimethylether,



prepared from the unsymmetrical tetroxybenzene differs completely from the monomethyl iretol. Hence, the latter conforms to one of the two formulas:



Constitution of Iridenin and Iridin.—Iridenin has the formula $C_{16}H_{14}O_8$. By hydrolysis it takes up three molecules of water and breaks up into



Iridin, also, can undergo hydrolysis.

The presence of two phenol groups in irigenin is demonstrated by the formation of the dibenzoylirigenin and the diacetylirigenin; the unstability of diacetyl derivative relative to the

monoacetyl derivative, indicates that these phenol groups are not similarly situated in the irigenin molecule.

We have not yet been able to crystallize the hydrolyzed irigenin, but, by converting it into its potassium or sodium salt (accomplished by treating its absolute alcohol solution with sodium or potassium ethylate) we have thus been able to effect its isolation. From the analysis of these salts is made clear the reaction of the hydrolysis.

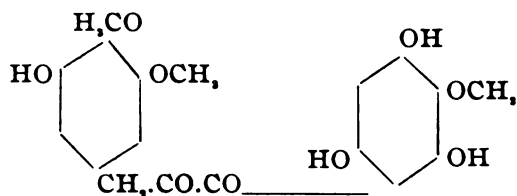
ANALYSIS.

($C_{24}H_{28}K_3O_{14}$ and $C_{24}H_{28}Na_3O_{14}$.)

| | Per cent. K. | Per cent. Na. |
|-----------------|--------------|---------------|
| Calculated..... | 17.96 | 11.39 |
| Found..... | 18.32 | 11.69 |

If, now, instead of using an *excess* of potassium ethylate, only the amount sufficient to form the tribasic salt be taken, a *di*-basic salt is always the result, which indicates that one of the hydroxyl groups of the hydrolyzed irigenin is of a weaker acid character than the other two. Consequently, the first product in the hydrolysis of iridin is $C_{18}H_{14}O_4(OH)_2(OC_6H_{11}O_4)_2$, and, for irigenin, is $C_{18}H_{14}O_4(OH)_4$.

Since the hydrolyzed irigenin is a relatively stable compound, not being attacked by reagents which effect the saponification of ether, we conclude that the two portions of the irigenin molecule, representing respectively iridinic acid and iretol, are not linked together by an oxygen atom, but are held together by a chain of carbon atoms, as shown in the following formula :



According to this formula, the hydrolyzed irigenin is an α di-ketone. This is further proved by the similarity of its reactions with alkali reagents and those of benzene, the latter, in the presence of potassium cyanide, yielding benzaldehyde, and benzoic acid, while the former yields iridinic acid, or aldehyde, and a carboxyl derivative of iretol.

This is more particularly shown by the formation of the same aldehyde by the decomposition of irigenin, and also synthetically from iretol. In the first case, the hydrolysis of the irigenin was effected by dilute caustic soda. After precipitating with sulphuric acid and filtering, soda solution and potassium cyanide were added to the solution. After standing some eight days, it was acidified and extracted with ether. The aldehyde was separated from the ether extract by sodium bisulphite. By cautiously decomposing with sulphuric acid, and shaking with ether, the aldehyde was obtained as a syrup, which, on digesting six hours with alkali, gave the theoretical amount of formic acid.

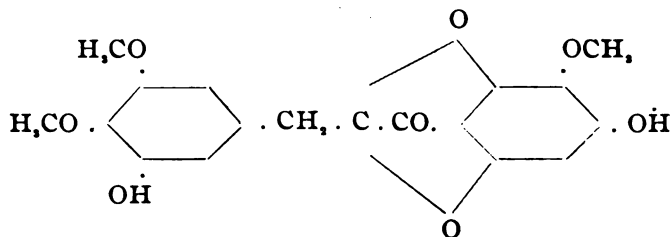
The synthesis of the aldehyde from iretol was effected by the action of chloroform and caustic soda on iretol in an atmosphere of hydrogen. After removing the chloroform by evaporation, the aldehyde was separated as above, it was also, in like manner decomposed, yielding iretol and formic acid.

The hydrolyzed irigenin, by taking up the elements of water, breaks up into iridinic acid and iretol aldehyde, this latter subsequently being converted into iretol and formic acid. Analogous to this is the decomposition of phloroglucinolcarboxylic acid into phloroglucinol and carbon dioxide, by boiling its aqueous solution.

From the foregoing, we feel justified in giving irigenin the formula

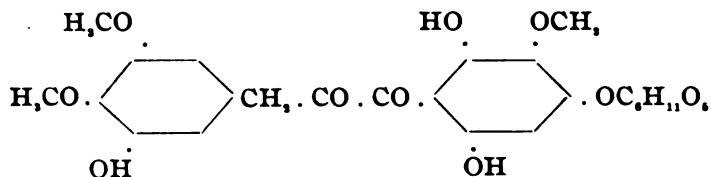


The irigenin itself contains one less molecule of water, and, in accord with all the reactions described, has the following constitution:

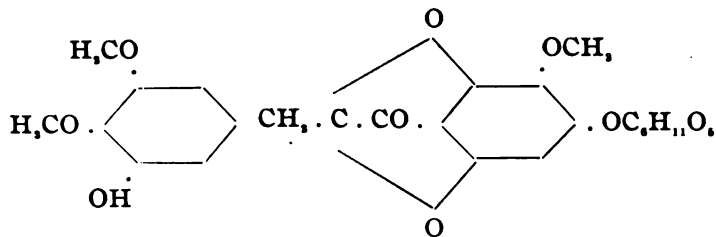


The iridin contains the glucoside residue, $OC_6H_{11}O_4$, in place of one of the two hydroxyls of irigenin.

We have previously noted the weaker acid character of one of the three hydroxyls of hydrolyzed iridin relative to the other two; we have also remarked that in titrating iridinic acid; $(H_2CO)_3.C_6H_4(OH)(CO_2H)$, with caustic soda and litmus, the end-point is obtained as soon as the hydrogen of the carboxyl group has been replaced by the alkali. From these two considerations we conclude that in the hydrolyzed iridin, the hydroxyl having the weakest acid character is found in the iridinic acid nucleus. Consequently, the constitution of hydrolyzed iridin is



Finally, if the above results and conclusions are correct, iridin itself has the constitutional formula



In closing, we would add a word regarding the probable relation of iridin and irigenin to the sugars; both are carbohydrates, and, as without doubt, the sugars are the first products changes of the plant matter, it appears probable that iridin and irigenin are formed from three and four molecules of sugar respectively, by the splitting off of eleven and ten molecules of water. In reviewing the possible methods of the formation of sugars from benzene derivatives, our attention is called to "cyclo" sugars, formed by an aldol condensation between the first and sixth groups of the chain in hexanpentolal



This, perhaps, is the manner in which inosite is formed. Since the pinite occurring in some resins has been proven by L. Maquenne¹ to be the monomethyl ether of an inosite, and, as the latter, by the symmetrical splitting off of three molecules of water, yields phloroglucinol, and the former, by losing two molecules of water, yields dihydroiretol, which can be converted into iretol by the removal of two atoms of hydrogen, the general relation of iridin to the sugars is better understood.

Our thanks are due to Dr. Paul Krüger, and to Dr. Richard Schmidt, for their valuable assistance in prosecuting this investigation.

BOTRYTIS BASSIANA AND ITS CRYSTALLINE PRODUCTS.²

BY E. VERNON.

AMONG the alterations produced by *botrytis bassiana* almost all authors note an abundant crystalline efflorescence which very often covers the small mummified bodies of the muscardin worms.

M. Dandolo in note 21 of his book, "*L'Art d'élever le ver à soie*," 1814, has written on this subject as follows: "As soon as I had observed attentively the worms or muscardin chrysalides I affirmed without hesitation that all this must be the consequence of chemical attractions and combinations."

It was in fact difficult to be mistaken after having seen the animal tissue altered in this manner and converted into a substance more or less hard and unalterable while before it was an animal substance easily decomposed. I put away with care the white saline substance which enveloped the so-called muscardin worms and afterwards analyzed it. Not being satisfied with my work I asked my learned friend, M. Brugnatelli, professor of chemistry at Pavia, to make an analysis of the material.

"The muscardin which covers the mummy of the worm or the chrysalide in the cocoon is composed principally of magnesium ammonium phosphate."

A like opinion was given by M. Lomeni (*Variétés agraires*

¹ *Ann. chim. phys.*, [6], 22, 264.

² Read before the World's Congress of Chemists, Thursday, August 24, 1893.

économiques et technologiques, 3, 1835), who says: "The chemical analysis of this substance has proved to M. Dandolo and to the late Professor Brugnatelli that the efflorescence of the muscardin is a combination of magnesia, phosphoric acid, and ammonia. " Professor Balsamo thinks also that the whitish efflorescence by which the worms are enclosed is entirely inorganic."

Mr. Charles Vittadini in his celebrated work, *Della natura del calcino o mal del segno* (*Journal de l' T. R. Istituto Lombardo di Sc. L. A.*, 3), expresses an entirely different opinion on this subject.

"The cadavers of the muscardin worms," he says, "after being deprived of their efflorescence and kept in a humid state become covered, after several days, with a second efflorescence which has also the appearance of a muscardin; but this is formed by myriads of fine crystals produced by the final chemical metamorphosis of the cadaver. These crystals observed by the naked eye have the form of diverging bunches of needles like a brush or of rounded masses which resemble the sea-urchin. They are transparent, colorless, or slightly reddish. The crystals dissolved in warm water show a decidedly acid reaction which becomes more sensible by evaporating the solution; on being treated with caustic potash it gives off a strong ammoniacal odor; the geometrical figure consists of long prisms with a rectangular base with cuneiform extremities."

"The reaction obtained by M. Cardoné on a small quantity of the crystals indicates a combination of alloxanic acid and ammonia with small quantities of potassium and calcium. In fact during the new process of crystallization a thick reddish liquid, generally alkaline, of a strong ammoniacal odor, flows off the cadaver of the worm and deposits a considerable quantity of crystals."

This secondary efflorescence, which takes place not only on the surface of the cadaver but extends to all the interior tissues by giving them an almost vitreous appearance, explains to a certain extent the doubt expressed by some observers that the *botrytis* is nothing else than simple crystallization.

I cite only these three authors who agree with what the literature furnishes on the nature and composition of the efflorescence

and do not mention others who have investigated the crystalline efflorescence and its different properties.

The worms mummified by the muscardin, consist always of a plentiful crystalline substance which, dispersed between the tissues, is accumulated in considerable quantities in the interior of the different parts of the somatic cavity. But it is to be remarked that the crystals do not always have the same exterior appearance; this depends on the humidity of the surrounding atmosphere. When kept perfectly dry from the beginning the crystalline substance remains inside of the cutaneous integument and consists of very fine needles which impregnate all the tissues. In an atmosphere more or less humid the cadaver when it begins to dry, exudes on the surface a dense reddish humor, which has the appearance of a crust of an earthy appearance. The microscope shows that the exuded substance notwithstanding its amorphous appearance is mostly of a crystalline nature and is not different from the substance left and dispersed between the interior viscera.

Finally, if we place the fresh cadaver in a warm place, more or less closed and saturated with moisture we will see at a certain time the crystallization in the sea-urchin form rupture the superficial integument. Often they are distributed without order in different parts of the body but generally may be found in both extremities and where the visceral volume does not hinder a larger expansion of the somatic cavity.

It is to be remarked that the formation of the sea-urchin crystallizations is not limited to the time immediately following the death of the worm. I was able to obtain it from cadavers mummified some months before by placing and keeping the cadaver during some weeks in a humid warm place. By means of needles these crystals can be removed from the cadaver like stone from a dried fruit.

By this method I was able to provide myself with a considerable quantity of material though not free from mechanical impurities and of reddish appearance. By dissolving it in warm water filtering, and concentrating the filtrate at a moderate temperature I obtained a crystalline mass which on being redissolved, recrystallized two or three times, and separated from the mother liquor, were obtained perfectly pure. I may remark here

although the warm water is of a moderate temperature (50° – 60° C.) the solution of the crystals is always accompanied by the formation of very small bubbles which are probably carbon dioxide; in repeating this operation an insoluble residue always perceptible though very light is noticed. This is the reason which led us to believe that the crystals are not stable and liable to decompose even by dissolving in distilled water. That belief is fortified by the fact that I was never able to obtain the crystals in the sea-urchin form though under the microscope the crust of the second and third crystallization seemed to be composed of ordinary prisms with dihedral extremities.

The crystals of the sea-urchin form are easily soluble in distilled water and react decidedly acid. Dried and heated in a small test-tube which is covered by a piece of paper moistened with litmus solution they produce the following phenomena: without any visible change of appearance, they expel ammoniacal vapors which turn the litmus blue; by further heating they melt to an ash-colored, foamy mass, the bubbles expelling whitish vapors. On the neck of the tube small drops of a condensed liquid can be seen; in the upper part of the test-tube a ring of crystalline needles sublimes; the odor is strong and excites a cough; on the bottom remains a whitish compact residue with little carbon.

The solution obtained from the crystals does not show any change with hydrochloric and sulphuric acids; ammonium chloride, ammonia, and sodium phosphate form an abundant precipitate. Ammonium carbonate and caustic ammonia do not produce any visible reaction.

The solution remains clear on concentrating with platinum chloride or even with potassium antimoniate; calcium hydroxide sets free an abundant quantity of ammoniacal vapors. The residue left from evaporation on the salt-bath dissolved in nitric acid produces some insoluble flocks; the result is almost absolutely negative with molybdic acid.

Another portion of the liquid was treated with barium chloride and gave an abundant precipitate, soluble in hydrochloric acid; a white precipitate is obtained by treating with silver nitrate; calcium chloride gave a white precipitate on being added to the

alkaline solution; ferric chloride precipitates voluminous reddish flocks.

A portion of the solution of crystals obtained was precipitated with lead acetate; the precipitate was decomposed by hydrogen sulphide; the filtered solution after evaporating, left on the bottom rhombic prisms which, on redissolving, produced a white precipitate with calcium chloride insoluble in acetic acid. Heated in a small tube they sublime without residue, while heated with strong sulphuric acid they effervesce and evolve carbon dioxide and carbon monoxide.

Finally I investigated the residue of the calcined crystals of the sea-urchin form. This, when dissolved in hydrochloric acid, does not give any appreciable precipitate unless by adding ammonia, ammonium chloride, and sodium phosphate. After all the reactions I have mentioned above there can not be any doubt about the composition of the crystals. Not taking into consideration the impurities which can not be entirely removed and remain as undeterminable traces of potassium, phosphoric, silicic, and succinic acid, the crystals are composed mostly of *oxalic acid, ammonium, and magnesium*.

I have also determined the percentage composition of the crystals as completely as the small amount of material permitted.

I. Purified crystals, 0.0784 gram; dried at 100° C., 0.0686 gram; difference = 0.0098; equal to 12.47 per cent. Dissolving the crystals in distilled water and treating the acidified solution with calcium acetate I obtained by the regular method 0.054 gram calcium carbonate which corresponds to 0.0389 gram oxalic acid or 49.62 per cent.

II. Purified crystals, 0.2572 gram; dried at 100° C., gave 0.2243 gram; difference 0.0329, equal to 12.80 per cent. Dissolved in distilled water and treated with calcium acetate gave 0.1727 gram calcium carbonate which corresponds to 0.1243 gram oxalic acid or 48.33 per cent.

III. Purified crystals, 0.1571 gram; dried at 100° C., 0.1376 gram; treated with milk of lime (Schloesing's method). After forty-eight hours the ten cc. of normal sulphuric acid was neutralized by only 8.06 cc. of normal caustic soda or 1.94 cc. of

normal sulphuric acid was neutralized by the ammonium of the crystals, which corresponds to 22.23 per cent.

IV. Purified crystals, 0.2560 gram; dried at 100° C., left 0.2243 gram; Schloesing's method for determination of ammonium gave 0.0576 gram of ammonium, equal to 22.50 per cent.

V. Purified crystals, 0.0789 gram; dried at 100° C., left 0.0690 gram. The hydrochloric acid solution precipitated with ammonium chloride, ammonia, and sodium phosphate, gave 0.0066 magnesium pyrophosphate, equal to 0.0015 magnesium or 1.9 per cent.

After the above determinations I conclude that the sea-urchin crystals of the muscardin after being purified by repeated crystallization, contain on an average:

| | Per cent. |
|------------------|--------------|
| Water | 12.635 |
| Oxalic acid..... | 48.975 |
| Ammonium | 22.365 |
| Magnesium..... | 1.900 |
| | <hr/> 85.875 |

I regret that the amount of material was not sufficient for further investigations in order to find the fourteen per cent. necessary to complete the analysis. We could then establish whether the crystals contain any water which is separated at higher temperature than 100° C. We could also determine the carbon dioxide given off while dissolving the crystals in water and ascertain from comparative analysis the products of different successive crystallizations.

Nevertheless I believe the data we possess are sufficient cause to accept in full certainty that the crystals represent a double salt of oxalate of magnesium and ammonium.

I find described in the literature five double oxalates of the following formula of constitution:¹

1. $C_2O_4Mg, 7C_2O_4(NH_4)_2 + 8H_2O$.
2. $3(C_2O_4Mg), C_2O_4(NH_4)_2 + 2H_2O$.
3. $C_2O_4Mg, 6C_2O_4(NH_4)_2 + 9H_2O$.
4. $5(C_2O_4Mg), 13C_2O_4(NH_4)_2 + H_2O$.
5. $C_2O_4Mg, 5C_2O_4(NH_4)_2 + 10H_2O$.

of which the percentage compositions are as follows:

¹ Souchay et Lenssen, Kayser in *Poggend. Ann.*, 60.

866 BOTRYTIS BASSIANA AND ITS CRYSTALLINE PRODUCT

For the first formula :—

| | Per cent. |
|-----------------|-----------|
| Oxalic acid.... | 63.30 |
| Magnesium | 1.08 |
| Ammonium | 22.66 |
| Water | 12.95 |

99.99

| | For the Second,
Per cent. | Third,
Per cent. | Fourth,
Per cent. | Fifth
Per cent. |
|------------------|------------------------------|---------------------|----------------------|--------------------|
| Oxalic acid..... | 76.52 | 61.23 | 62.26 | 58.6 |
| Magnesium | 7.82 | 1.19 | 2.36 | 1.3 |
| Ammonium | 7.82 | 21.47 | 18.40 | 20.0 |
| Water..... | 7.82 | 16.10 | 16.98 | 20.0 |
| | 99.98 | 99.99 | 100.00 | 99.9 |

Comparing the results obtained from our analysis with figures we have to exclude without hesitation formulas 2 in which there is a considerably larger amount of magnesium than we have found. Taking into consideration the fact mentioned on the first pages of this investigation, that the crystals radiated from the muscardin worms are partly composed by dissolving in distilled water and the phenomenon which this decomposition is accompanied I believe there is no doubt that the essential cause of the change must be in the oxalic acid.

But as oxalic acid is rapidly diminishing the amount of ammonium and magnesium must increase in the products of renewed crystallization.

This consideration compels me to lay aside also formulas 1 and 3 and prefer formula 5 as more nearly approaching the results obtained than any of the others.

I have already emphasized at the beginning of this work that the crystals of the sea-urchin form whose nature I have elucidated, are only formed under certain circumstances. But if we enclose the cadaver in a warm and humid place we can contrary determine their development at our will.

It seems to me that this fact authorizes us to make an interesting conjecture; namely, that the immediate action of the *botrytis* is limited to the production of oxalic acid. The ammonium remains principally free, being combined generally with small quantities of lime and magnesia.

But if the surrounding circumstances produce the putrefaction of the cadaver and the development of ammonia, ammonium

oxalate is formed at the same time, which dissolves a certain amount of magnesium oxalate forming the double oxalate; only it then forms that peculiar crystallization to which we wished to confine our attention.

It is very remarkable that *botrytis bassiana* cultivated on nutritive gelatine produces oxalic acid in large quantities which I have separated in a crystalline form.

**CLOSING ADDRESS DELIVERED BEFORE THE WORLD'S
CONGRESS OF CHEMISTS, AUGUST 26, 1893.**

BY ALBERT B. PRESCOTT.

I N this closing hour of the Congress the chair would congratulate its members upon the great interest and value of its transactions. In the wide attendance of European and American chemists, in the weight of the papers in the several divisions of chemical science, in the constant and increasing attendance through the sessions of six crowded days, and in the hearty spirit of brotherly sympathy which has given life and happiness to all our labors, we have been favored beyond the most sanguine expectations. We in the United States know the chemists of Europe better than we did before this Congress. Surely we have the best of encouragement for the union of the chemists of the world in a series of great meetings of profit and acquaintance, the first one of which is now being concluded.

I know that I voice the sentiment of every member when I give our united thanks to those whose active and untiring exertions have carried so well all the arrangements of this meeting. Our thanks are due, first, to the American Chemical Society, who instituted the call for the Congress and now opens its journal to our proceedings. To our general chairman of the joint committee, Professor Wiley, of the United States Department of Agriculture, we have been indebted for most efficient attention in details. He took the position when it was not easy to find one to accept its labors and to face its uncertainties. The chairman of the committee on papers, Professor William McMurtrie, and assuredly the chairman of the committee from the Congress Auxiliary, Professor John H. Long, the local

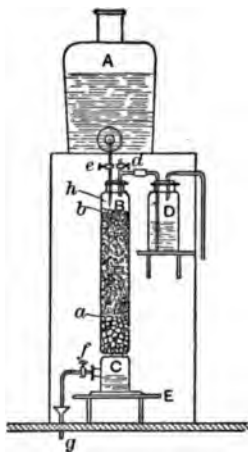
genius of our convention, will be remembered most gratefully by us all. I will not longer detain you from your personal farewells to each other, and now declare the Congress adjourned.

HYDROGEN SULPHIDE GENERATOR.

BY H. G. SCHANCHE.

Received September 13, 1894.

THE form of generator shown in the annexed cut has proved itself, during seven years of use, to always furnish an *absolutely uniform supply of gas*.¹ The acid reservoir A delivers the acid into the generator B, containing ferrous sulphide, *a b*, resting on coarse pebbles at *a*. The ferrous chloride collects in C and may be drawn off, from time to time, by opening cocks *d* and *f*, thus allowing it to flow through the lead pipe *g* into a drip-pan underneath the table; D is an ordinary bottle for washing the gas. By regulating the flow of acid by means of the cock *e*, any supply of gas may be obtained, while the height of the column of ferrous sulphide, through which the acid percolates, assures an absolutely uniform supply of gas, as well as a complete neutralization of the acid. The shelf E, on which the generator B rests, can be slipped off its bracket, thus facilitating the removal of B for cleaning or charging.



[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY, U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY, NO. 11.]

MODIFICATION OF KNORR'S EXTRACTION APPARATUS.

BY OMA CARR.

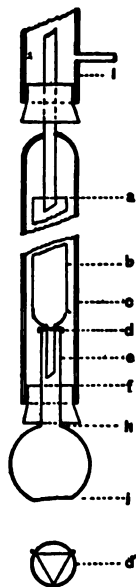
Received October 15, 1894.

TO avoid the inconveniences found with the usual form of mercury seal extractors,¹ such as the expense of flasks, disturbance of the seal by unequal pressures, tendency of the mercury to enter the flask, etc., the modification shown in the drawing is suggested.

The tube *a b* may be of any convenient size adapted to the

¹ Bulletin, No. 28, Division of Chemistry, p. 97.

inverted percolator-dome c. The top of the flask neck may be simply rounded in the flame, and the small triangle d d' arranged to support the shoulder of the tube a b. The length of the flask between points d and h may be any desired distance, but it is suggested that it protrude above the cork f two inches. The cork f requires no previous extraction, as the solvent in contact with it can not enter the flask containing the extract except by volatilization. The flask may be of any desired size, although the ordinary "sugar flask," of 100 cc. capacity, without rim at the mouth, will be found convenient for the greater range of work.



Where it is desired to complete extract solutions to a definite volume the arrangement will be found particularly useful. The apparatus should be sunk in a water-bath to a depth sufficient to prevent accumulation of the solvent upon the cork f. The apparatus is simple and readily adapted to the condenser of the Knorr extractor, shown at l.

Upon completion of the extraction, the cork f is easily removed and the flask wiped and dried without danger or annoyance caused by mercury globules.

LABORATORY DEVICES.

By ELWYN WALLER, PH.D.

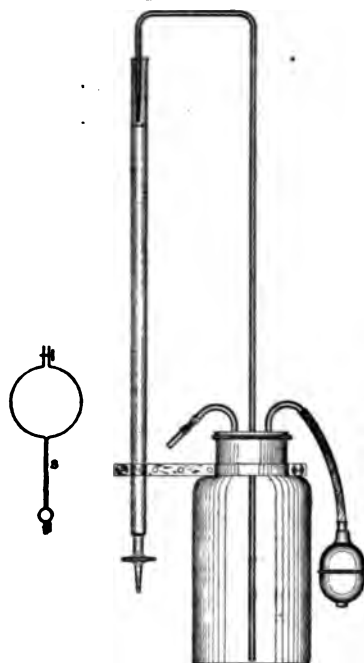
Received October 17, 1894.

DURING the recent general meeting of the Society in Brooklyn, many of the members visited the mineral water establishment of Dr. C. H. Schultz, in New York, and enjoyed his hospitality. After the lunch, the different parts of the plant were inspected by the visitors. In the analytical laboratory were a few forms of apparatus which attracted much attention as they have heretofore not been described. These were the burette-filling device, designed by Dr. A. P. Hallock, the chemist of the factory, the condenser and revolving Nessler rack, adapted by E. W. Martin, of the New York Health Department, and the Nessler comparator as improved by Dr. Hallock.

A description of these may be of service.

BURETTE FILLER.

Around the neck of a bottle of convenient size for the stock solution (capacity two liters or more) is fixed a collar of brass,



carrying a clamp for the burette. The collar and clamp are made of two strips of brass bent as shown in the sketch, which are soldered or riveted together at s. The ends are turned outward, and fitted with thumb-screws, to allow the circles to be clamped firmly about the bottle neck and the burette.

The (rubber) cork of the bottle is pierced with three holes. Through one of these passes a tube extending from near the bottom of the bottle to above the top of the burette, then, turning twice at right angles it dips into the burette, being steadied in position there by a cork with a small slit on one side, or fitting loosely. The end of this tube is

a little constricted, and cut off at a point corresponding with the zero line of the burette graduation.

Through another hole in the cork passes a short tube connected with an ordinary syringe compression bulb, by means of which air can be forced into the top of the bottle.

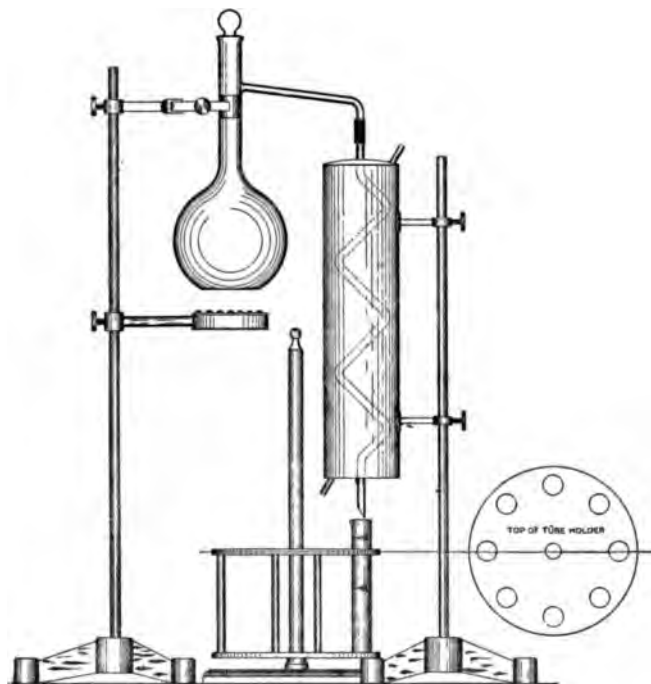
Through the third hole passes another short glass tube, the external end preferably bent downward, so that it may be easily closed by the finger when it may be desired to compress the air in the bottle, or by taking the finger away, the pressure may be at once released.

When it is desired to fill the burette, by closing the air-tube with the finger, and squeezing the bulb a few times, the stock solution is forced over into the burette. As soon as the level of the liquid has come to or above the zero line, the air pressure is released by removing the finger, and all the liquid above the

zero mark siphons back into the stock bottle, leaving the burette filled to the zero mark and ready for use.

The device is simple and comparatively inexpensive, and it has the great advantage that the delivery ("nose") of the burette can be easily fixed at a convenient height above the working table.

Serious objections to most other forms of apparatus constructed for this purpose are, that the delivery of the burette is too high above the working table, or that the stock-bottle has to be fixed



in some elevated position, or that the form of burette which must be used is an elaborate and costly piece of glass-blowing.

CONDENSER.

For water analysis distillations, etc., a glass-stoppered flask with side-neck tube is used. The end of the side-neck tube is turned vertically downward, being thrust deeply into the tin tube of the condenser, and held in place there by a short piece

of rubber tubing. The three-eighths inch block tin pipe the condenser-tube is bent zigzag instead of in the conventional helix. This affords a more even flow of the distillate. The cylindrical copper jacket containing the water for cooling is about 3 inches in diameter, and fifteen inches long. The disk at the lower end is *arched upward* so that in case the condenser "sweats" from the use of very cold water, the drip from outside can not contaminate the distillate. The lower end of the tin tube is cut aslant for the more certain delivery of the distillate.

REVOLVING NESSLER STAND.

This is simply a whirlingig rack made of two circular boards connected with light strips of wood, the upper circular board perforated to carry eight or ten tubes, the lower partly perforated to form shallow sockets for the tubes. The rack revolves about an upright set in a base. With such a stand as this, if one tube is placed in position to receive the drip from the condenser, revolving the rack will bring successively every tube on the stand into the same position. The danger of tipping or breaking the tubes is practically eliminated, and over, the order in which the fractions of the distillate are taken off is easily preserved.

NESSLER COMPARATOR.

This has the form of a large test-tube rack of wood, painted black.

At the bottom is placed a strip of milk glass, extending end to end, held in place by small pieces of rubber (or small rubber cork) fastened to each side by small screws. The edges of the rubber are put so close to the bottom board that the glass can be just forced in between, and when in place is firmly held.

About two inches above this is a strip of clear glass held on cleats at the sides of the rack, fixed in place in the same manner as above described, and upon this clear glass the tubes stand. The necessity for raising the tubes from the black background, in order to make a comparison is thus obviated, and the whole apparatus may be very readily cleaned and

condition. The drawbacks in the use of white paper for a background which may be easily wetted or stained are removed.

It has been found convenient to use a rack of ten or twelve holes, since with that the standards can be placed in every other hole, leaving the vacant spaces for the tubes to be compared.

NEW BOOKS.

LESSONS IN QUALITATIVE AND VOLUMETRIC CHEMICAL ANALYSIS FOR THE USE OF PHYSICIANS, PHARMACISTS, AND STUDENTS. BY DR. CHAS. O. CURTMAN; INCLUDING LESSONS IN QUALITATIVE CHEMICAL ANALYSIS, BY DR. F. BEILSTEIN. Fourth edition. St. Louis, Mo.: John L. Boland Book and Stationery Company. 1894. Price \$1.50.

This new edition of a work intended primarily for students of medicine and pharmacy, contains chapters on manipulations of chemical apparatus, qualitative analysis (inorganic), examples for practice in the analysis of organic substances (proximate), volumetric analysis, examination of drinking water, and urine analysis. The author says the section on volumetric analysis "contains numerous examples illustrating every important volumetric method and forms a complete commentary on the volumetric assays of the new U. S. Pharmacopeia." The book contains a number of cuts illustrating various forms of apparatus, urinary sediments, several pathologic micro-organisms, and two charts of spectra. Meyer and Seubert's atomic weights are used. "The orthography has been adapted to the rules of the Chemical Section of the A. A. A. S."

To cover so large a part of the domain of analytical chemistry within a space of 300 octavo pages has required the constant and severe abridgment of methods allowing no opportunity for a discussion of their merits. The author has accomplished his purpose with more than ordinary success. As a rule he has shown excellent discrimination in the choice of methods, and has in some cases introduced matter one would hardly expect to find in so small a work, *e. g.*, Gutzeit's, Fleitmann's, and Bettendorf's tests for arsenic. Physicians and pharmacists will doubtless find the work a useful one. In some cases brevity of treatment has led to dogmatic statements that are liable to be wrongly interpreted by those having little knowledge of the subject under

discussion. Examples of this kind may be found in the chapter on the examination of drinking water. One having had experience in the matter would hardly be willing to state that "albuminoid ammonia may be considered as *proof of sewage actually present*, etc.," p. 244,—the italics are the authors. Other examples of a similar kind might be quoted. Standards of organic impurity in drinking water—a dangerous subject even for experts—can not be arbitrarily established, and the wise analyst will express a positive opinion only as he knows the history of the sample of water under examination. W. W. DANIELLS.

LABORATORY MANUAL OF ELEMENTARY CHEMICAL PHYSIOLOGY AND URINE ANALYSIS. BY JOHN H. LONG, M.D., Sc.D., PROFESSOR OF CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES IN THE SCHOOL OF MEDICINE AND PHARMACY OF NORTHWESTERN UNIVERSITY. Small 8 vo., pp. 360 and index. Chicago: E. H. Colegrove & Co. Price, \$2.50.

This work is a decided departure from the methods of the laboratory text-books usually offered to medical students. It joins the exercises in physiologic chemistry with those of applied medical chemistry, a plan that will increase the interest and value of the course. All through the book we find evidence that it is written from practical experience and is an evolution of years of teaching.

In the preface Dr. Long discusses briefly the unsatisfactory state of teaching at medical schools. He expresses the feeling growing among those engaged in teaching chemistry at such schools, that the general principles of the science should be made an entrance requirement.

The first part of the book, one hundred and seventy pages, comprises the chemical physiology. Methods of investigation are presented in considerable detail. Especially noticeable is the essay on polarimetry. Reference occurs as frequently in organic chemistry and physiology to rotation of the polarized ray, and the phenomenon is now recognized as having so direct a relation to molecular structure, that it is wise to give it full explanation. Numerous illustrations of the form and action of polarizing apparatus are given.

Part II, on Urine Analysis, comprises over one hundred and

sixty pages, and includes all that is required for the medical course.

We must express a regret that the spelling is old-fashioned. A teacher in a medical school may be excused from going to the full length of using "sulfate," "sulfid," etc., since the new pharmacopeia has refused to adopt these forms, but the useless final "e" might be dropped in many cases, and general usage permits the abandonment of the diphthong "æ" in all English words. We should prefer, therefore, "hemin" to "hæmin." It is pleasing to note that the approved term "glycerol" is used.

Several useful tables are included in appendix.

There are numerous illustrations of apparatus and of microscopic appearances of important structures. The work will be of great service in the field to which it is devoted. H. L.

THE CHEMISTRY OF PAPER-MAKING. TOGETHER WITH THE PRINCIPLES OF GENERAL CHEMISTRY. A HANDBOOK FOR THE STUDENT AND MANUFACTURER. BY R. B. GRIFFIN AND A. D. LITTLE. 8 vo. pp. 517, 99 illustrations. New York: Howard Lockwood & Co. 1894. Price, \$5.00.

The scope of this book is sufficiently indicated in the title. One hundred of the opening pages are devoted to elementary chemistry, evidently intended for the manufacturer who knows little chemistry or has forgotten it; perhaps this was necessary; for chemists who buy the book it is certainly superfluous. Regarding the remaining pages it may be said that the authors display practical as well as theoretical knowledge of the subject, and the result is an entirely satisfactory treatment. They seem to be investigators as well and have embodied in nearly every section some valuable matter derived from their own experience. This will be especially true of those sections of the book treating of the chemical analysis and of paper-testing, which, to most chemists, prove its most valuable features. The treatment of these sections is thoroughly common sense and shows both knowledge and good judgment. Fourteen pages are given to an account of cellulose and its derivatives and their properties; then we have thirty-four pages on the various fibers. Following this, seven pages are devoted to an account of the processes for isolating cellulose. Seventeen pages are given to the soda process,

one page to the sulphate process, and nearly 200 pages to the sulphite process. Next comes Bleaching, twenty-six pages; Sizing and Loading, nineteen pages; Coloring, nine pages; Water, nineteen pages; Chemical Analysis, seventy-two pages; Paper-Testing, thirty-two pages; Electrolytic processes, eleven pages, and an appendix and index. Among other things, the appendix contains an account of the interesting thiocarbonates of cellulose discovered by Cross and Bevan, and a list of United States patents relating to the sulphite process. In brief, the book is an excellent one: well written, well printed, and well illustrated, and worthy of a place on the book-shelf of the chemist.

E. H.

A SHORT HISTORY OF CHEMISTRY. BY F. P. VENABLE, PH.D. 12 mo. pp. viii; 163. Boston: D. C. Heath & Co. 1894. Price, \$1.00.

The author, who is Professor of Chemistry in the University of North Carolina, has, for several years, given lectures to his students on the history of chemistry, and this little volume is an outgrowth of those lectures. The subject is divided into six Parts: I. the Genesis of Chemistry; II. The Alchemists; III. Qualitative Chemistry; IV. Quantitative Chemistry; V. Structural Chemistry; VI. Special Branches of Chemistry. Each Part is subdivided into unnumbered sections and paragraphs, with headings in bold-faced type, making the book convenient for study.

Considering the limited space in the book, the author has certainly arranged an accurate compendium for chemical students, covering the entire field. He shows knowledge of the standard works on historical chemistry in three languages, but he appears not to have access to the earlier original works, except in a few instances. Viewed in the light of the original writings of the zealous alchemists, the iatro-chemists, and the learned philosophers of the last century, the history of chemistry becomes as fascinating as a romance, and a work based on them acquires an individuality which is only partly reflected in a compilation at second-hand.

We notice that high honor is paid to the erudition of the Arabian chemist, Geber, notwithstanding Berthelot has shown that the writings usually ascribed to Geber can not be traced

back farther than the beginning of the XIII century, and that they never did exist in Arabic; the MSS. said to be found in the Paris Bibliotheque Nationale and which have been translated into Latin and modern languages are fictitious.

In a larger part of the volume the subject is treated in a series of biographies; this, however, is natural where the discoveries of certain individuals exerted radical changes in the philosophy of the science.

In Parts IV and V the development of modern chemistry is well set forth, and every student of the science would do well to read and absorb these chapters early in his curriculum.

Professor Venable names a chemical periodical established as early as 1697 by Stahl.

An excellent feature of the work is its fair-mindedness, giving credit where credit is due. This remark is, perhaps, superfluous, as the book is American; but after Jagnaux' great volumes, written to prove that chemistry is a French science and the polemical writings of certain German authors, one can not but recognize the impartiality characteristic of American writers.

A few illustrations, portraits, and representations of original apparatus would have enlivened the volume; perhaps these can be introduced in a second edition. The proof-reading is excellent. There is an index.

H. C. BOLTON.

• **QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS.** BY DR. ALEXANDER CLASSEN. AUTHORIZED TRANSLATION, SECOND ENGLISH, FROM THE THIRD GERMAN EDITION, REVISED AND GREATLY ENLARGED. BY W. H. HERRICK, A. M. New York: John Wiley & Sons. 1894. Price \$3.00.

It is now twelve years since Professor Classen published the first edition of this book. The little volume of about fifty pages contained a systematic description of the methods then practiced in the laboratory at Aachen, little or no attempt being made to include the results that had been obtained elsewhere. An entirely rewritten and much enlarged second edition was issued in 1896. In this, electrolytic analysis is treated as an independent branch of quantitative analysis, but while the methods proposed and worked out by the author and his associates are fully presented, only occasional reference is made to the researches of

other experimenters: "Nach eignen Methoden," still remained the device of the book.

A third edition, of which the subject of this review is a translation, appeared in 1893. The author now evidently attempts to present a complete treatise on electrolytic analysis. The numerous controversies with other chemists, and the adverse criticism of some of his methods, have induced him to revise and modify considerable portions of the text, and to introduce many methods developed and described by others. Nevertheless the book is not entirely free from the defects of its earlier editions. Especially is it to be regretted that Prof. Classen has not thought it worth his while to give references to the original papers.

The most satisfactory part of the work comprises the introductory chapters; the descriptions of the apparatus used for generating, reducing, and measuring the current are very complete, and leave little to be desired. The Gilcher thermopile might, perhaps, have replaced the older constructions, and some of the obsolete forms of galvanic cells might have been omitted. The translator has made some very judicious additions, describing devices used in American laboratories.

Under "Determination of the Metals" much new matter has been introduced. Great stress is laid upon the proper control of the current, and, whenever possible, the normal density is given. Most of the space is allotted to the precipitation of metals from solutions of their double oxalates, and it is tacitly assumed, that this is in most cases the best method. Prominence is also given to the electrolysis of the sulphosalts of antimony and tin—a method improved by Classen—and the deposition of metals from solutions of their pyrophosphates (Brand). The names of Smith and Rüdorff appear very frequently, but we do not find that the directions for carrying out their processes are always adequate, and not a few of the American chemists' methods are entirely omitted.

This criticism applies even more strongly to the section on the separation of the metals. While excellent results are doubtless to be obtained by the use of many of the methods described here, it can not be denied that some are not separations at all (iron from cobalt, nickel, and zinc, etc.), and others are not

electrolytic separations. It seems to us that in many cases the author could have substituted, with advantage, the electrolytic processes, which have been proposed by others in recent years.

Professor Herrick's translation is excellent in every respect; while it closely follows the original text, it contains numerous very valuable additions.

H. F. KELLER.

LABORATORY MANUAL AND PRINCIPLES OF CHEMISTRY FOR BEGINNERS.
BY GEORGE M. RICHARDSON, ASSOCIATE PROFESSOR OF CHEMISTRY IN
THE LELAND STANFORD JUNIOR UNIVERSITY. pp. 233. New York:
Macmillan & Co. 1894. Price \$1.10.

This book is, as the author states in his preface, "principally intended as a *laboratory manual*," and the course of experiments "arranged for the elementary students of chemistry in this university." It is in two parts, Part I (pp. 84) consisting of a course of laboratory experiments, and Part II being devoted to theoretical chemistry.

While many of the laboratory experiments contained in Part I are instructive and well adapted for their purpose, and well suited for beginners, there are also many with which fault may be found.

In some instances these experiments involve the use of rather complicated pieces of apparatus requiring an expenditure of the student's time to get together and set up which is out of proportion to the importance of the fact to be taught by the experiment itself; in other instances the time and work required to perform the experiment are in like manner excessive when taken in comparison with the importance of its object.

But a far more serious fault than this lies in the difficulty of most of the quantitative experiments, of which there is a very considerable number, "greater," as the author states, "than is commonly found in such laboratory manuals."

Most of these quantitative experiments are decidedly beyond the ability of the average beginner in chemistry to perform with any degree of accuracy, and some of them can yield accurate results only in skilled hands.

It is far worse than useless to require a student to perform quantitative experiments without also requiring of him accurate results; hence, if quantitative work is to be given to the beginner

at all; in itself a matter of more than doubtful expediency; the experiments given him should be of the simplest kind only, and of such a nature that even in inexperienced hands, fairly accurate results may be obtained.

The requirement from students of quantitative work, the proper performance of which lies beyond their abilities, is almost inevitably followed by one of two consequences—the conscientious student, failing after repeated attempts to obtain correct results from an experiment, is apt to become discouraged, and begins to dislike his work; his less conscientious fellow, tiring of an experiment after he has repeated it once or twice, “cooks” his figures to give the desired result in order to get rid of it. In either case the harm done is great.

In Part II, “the writer has attempted to give a clear and concise statement of some of the fundamental theories and principles of chemistry; here he has gone more into detail than is customary in books designed for elementary students.”

This part is open to a similar criticism. Some of the matter it contains might be read with advantage by a beginner, but it is not in such form as to be readily available, and the consideration of such subjects as Absolute Temperature, The Determination of Molecular and Atomic Weights, The Determination of Formulas, The Kinetic Theory of Gases, etc., can scarcely be undertaken with profit by beginners in chemistry, and is also rather out of place in a book “principally intended as a laboratory manual.”

On the whole, while with some revision the book would be an excellent one to place in the hands of a second-year student, it is hardly one which can be recommended for the use of beginners.

R. D. C.

NOTES.

International Chemical Congresses.—The following circular letter has been addressed to the foreign chemical societies:

DEAR SIR:

An International Congress of Chemists, organized in connection with the World's Columbian Exposition, was held at Chicago in August, 1893. The American Chemical Society met

conjointly with the Congress, and, on account of the interest which was manifested, appointed a Committee of Conference to consider the expediency of holding similar congresses at regularly recurrent intervals of time. The geologists have established a series of International Congresses, which meet triennially; in medicine and pharmacy similar organizations exist; and in each case the success of the meetings has been very great. The undersigned, therefore, representing the American Chemical Society, respectfully request the chemical societies of the world to appoint similar committees of conference, in order to consider whether it is desirable and practicable to organize a series of International Chemical Congresses, in which the chemists of the various nations can regularly meet together for the discussion of questions of common interest. Hoping for a favorable response, we remain, in behalf of the American Chemical Society,

Very respectfully,

(Signed,)

F. W. CLARKE,
CHARLES E. MUNROE,
H. CARRINGTON BOLTON,
EDWARD HART,
W. O. ATWATER.

Please address reply to F. W. Clarke, U. S. Geological Survey, Washington, D. C., U. S. A.

Soldering Aluminum.—Professor Joseph Richards contributes an article on this subject to the first number of the *Aluminum World* from which we learn that the best results have been obtained from an alloy of zinc, tin, aluminum and *phosphorus*. "This solder can be used before the blowpipe or with a soldering iron. In the former case, a little silver can be added to it without making it too hard to melt, and giving it a better color. For use with the copper bolt, this solder leaves little to be desired. The surfaces to be united are first scraped clean, and then tinned with the solder itself by rubbing it on hard with the bolt. The prepared edges are then soldered together with ease, using a hot iron and no flux of any description."

Pure tin, or an alloy of tin and aluminum will solder, but the joints become brittle. Zinc and cadmium are useless because too brittle. Silver chloride attacks aluminum depositing silver,

and the surfaces thus formed may be soldered, but the material is too costly. Cadmium chloride can be used only when dry, and is a deliquescent salt. The Alsite aluminum solder is used only with the blowpipe; its composition is not divulged, and the melting-point is dangerously near that of aluminum. Electroplating the surfaces to be soldered is not satisfactory as the plating peels when subjected to heat. E. H.

Note on a Device for Weighing Oil for Analysis.—The following device I have for some time used, and found to be so convenient and simple, that I give a description of it hoping that it may be of service to others. It consists simply of a small glass evaporating dish, about one inch in diameter, supported upon a flat watch-glass. An amount of oil, greater than the amount desired for the experiment, is placed in the evaporating dish and the whole weighed. The proper amount of oil is then poured from the dish into the vessel in which it is to be analyzed, and its weight determined by difference. If a drop of oil should cling to the lip of the evaporating dish and run down on the outside, it will be caught by the watch-glass and will occasion no trouble. The whole affair costs but a few cents and may be cleaned with great ease, while for weighing oil it is quite as accurate as a weighing pipette.

November 5, 1894.

PARKER C. MCILHINEY.

ERRATA.—Page 348, May, 1894, ninth line from top of page, after the words *violent bumping*, insert *ninety cc. of water is now added*.

Page 349, May, 1894, in the last two lines, for *Cengola* read *Angola*.

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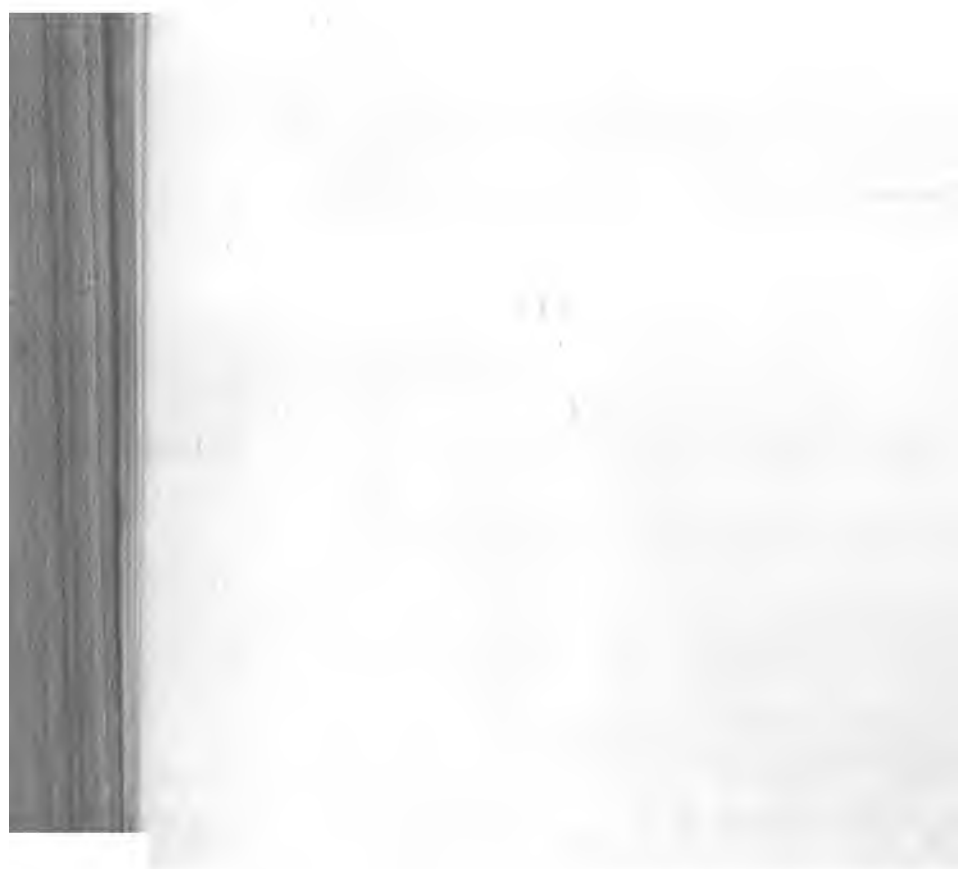
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Proceedings.

JULY 28, 1894.

In view of the fact that some members seem dissatisfied with certain provisions of the Constitution the President has been authorized by Council to appoint a committee to consider suggestions in regard to amendments to the Constitution of the Society.

NEW MEMBERS ELECTED JULY 17.

Anderson, J. T., Auburn, Ala.
Graham, W. H., 350 Central Ave., East Orange, N. J.
Hare, C. L., Auburn, Ala.
Kilmer, F. B., New Brunswick, N. J.
Lee, Isaac A., 162 Somerset St., New Brunswick, N. J.
McIlhiney, Parker C., School of Mines, Columbia College, New York, N. Y.
Miller, H. K., Auburn, Ala.
Noble, R. E., Auburn, Ala.
Parmly, Dalton, Oceanic, N. J.
Persons, Prof. A. A., Lake City, Fla.
Roeser, Frederick, care Globe Sm. and Ref. Co., Denver, Colo.
Slate, Wm. W., Bellows Falls, Vt.
Street, John Phillips, New Brunswick, N. J.
Taylor Duncan, care of Colgate and Co., Jersey City, N. J.

CHANGE OF ADDRESS.

Andrews, F. H., Box 476, Providence, R. I.
Bendinger, J. A., 6 Monroe St., Ann Arbor, Mich.
Bouton, Rosa, Chem. Dep't., State Univ., Lincoln, Neb.
Crobaugh, Frank L., No. 17 Bratenahl Building, Cleveland, Ohio.
Dohme, A. R. L., 301-307 W. Pratt St., Baltimore, Md.
Dorr, John V. N., Polytechnic Institute, Brooklyn, N. Y.
Drew, Dr. Chas. W., 505 Century Building, Minneapolis, Minn.

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Dunham, E. K., 358 E. 26th St., New York, N. Y.
Eager, F. D., Savoy, Neb.
Emmens, Stephen H., Amador City, Amador Co., Cal.
Escher, Paul, 212 E. Onondaga St., Syracuse, N. Y.
Farnsworth, John P., 26 Tobey St., Providence, R. I.
Ford, Allen P., 254 24th St., Detroit, Mich.
Geisler, J. F., Room 38, 6 Harrison St., New York, N. Y.
Genth, F. A., Jr., 103 N. Front St., Philadelphia, Pa.
Goodell, F. E., 1420 W. 12th St., Des Moines, Ia.
Hahn, A. G. C., 4 and 6 New Chambers St., New York, N. Y.
Harrington, E. M., Aetna, Lake Co., Ind.
Hawling, Henry H., 2135 L St., Washington, D. C.
Hays, Joseph A., care of E. M. Johnson Co., 98 William St., New York,
N. Y.
Hebden, John C., 40 S. Water St., Providence, R. I.
Hyde, Fred. S., Dep't. of Health, 40 Clinton St., Brooklyn, N. Y.
Johnson, Dr. S. W., Drawer 101, New Haven, Conn.
Krumme, John A., Jr., 800 Eastern Ave., Cincinnati, Ohio.
Lammers, Theodor L., 431 Chamber of Commerce Building, Duluth,
Minn.
Lee, C. Tennant, 146 Federal St., Boston, Mass.
McElroy, K. P., 1412 16th St., Washington, D. C.
Meeds, Alonzo D., Stillwater, Minn.
Menges, Franklin, Ph. D., Gettysburg College, Gettysburg, Pa.
Miller, John A., 203 Ellicott St., Buffalo, N. Y.
Mitling, E. K., 416 Huron St., Chicago, Ill.
Parmly Dalton, Sharpsville, Pa.
Quinan, Wm. R., Pinole, Contra Costa Co., Cal.
Richards, Joseph W., Ph. D., Lehigh Univ., Bethlehem, Pa.
Schiller, Louis J., Granite St., Am. Sug. and Ref. Co., So. Boston,
Mass.
Voorhees, Louis A., Box 290, New Brunswick, N. J.
Willard, J. T., Kan. State Agr. Coll., Manhattan, Kan.
Williams, W. J., 1412 Van Buren St., Wilmington, Del.
Wyckoff, George H., 1233 Washington, St., Kansas City, Mo.
Yount, Clarence E., 20 6th St., S. E., Washington, D. C.

THE BROOKLYN MEETING.

AUGUST 15 AND 16, 1894.

THE Brooklyn meeting was a very interesting one. The attendance was large, the papers numerous and interesting, and the excursions and social features successful and enjoyable.

The meeting was opened in the Chemical Lecture Room of the Brooklyn Polytechnic Institute on Wednesday, August 15, at 10 A. M., by Dr. Wm. McMurtrie, Chairman of the Committee of Arrangements, who briefly stated what arrangements had been made, and welcomed the visiting chemists. After a brief response by President H. W. Wiley, the Secretary made some announcements and stated that 728 names were now on the roll of members, and that of these only thirty-eight had not paid dues for the current year.

Dr. Wm. H. Hale presented through the Secretary, on behalf of the street railway companies, 500 trolley tickets for the use of members, for which a vote of thanks was passed.

The following papers were then read and discussed:

Contributions to the Chemistry of Cerium.

L. M. DENNIS and W. H. MAGEE.

Utilization of Acid Sulphates, particularly the so-called Niter

Cake of the Trade JOHN ENEQUIST.

Oxidation of Non-drying Oils by Air.....WALTER D. FIELD.

Oil-Gas.....W. A. NOYES.

Determination of Benzene in Illuminating Gas.....W. A. NOYES.

The Secretary announced that Dr. Wolcott Gibbs had been unanimously nominated by the Council for election to honorary membership in the society. Upon motion of Prof. C. E. Munroe, Dr. Gibbs was unanimously elected to honorary membership by a rising vote and the Secretary was directed to inform Dr. Gibbs of this action by telegraph.

The editor was called on for information about the JOURNAL and stated that considerably over 900 copies were now being sent out, only a few being exchanges. Probably 875 of these copies represent paid subscriptions, either of members or non-members. The number of subscribers who are not members is large and growing. The JOURNAL has been enlarged to seventy-two pages, and it has become necessary to reprint the January,

February, and March numbers, the first edition having been exhausted. A considerable amount of copy was now on hand and it would probably be necessary to still further enlarge the JOURNAL before the close of the year. Some further improvements were in contemplation but not yet ready for announcement. The greatest difficulty in the way of the Committee on Papers and Publications was in the lack of sufficient funds to print the material which came to the editor. He ventured to hope that members would bestir themselves in inducing proper persons to become members of the Society.

The President congratulated the members of the Society upon the good showing made. A charter for a Local Section had just been granted to the New Orleans chemists, and another section was in process of formation in San Francisco. With the present rate of increase the membership would doubtless exceed 1,000 before the close of the year. Chemistry has a great future in America. There is every reason to think that with proper effort we may have in this country the greatest chemical society the world has ever seen.

In the afternoon an excursion on the steamer "Blackbird" through the East river and adjacent parts of Long Island Sound had been arranged by the local committee. Stops were made at the Mineral Water Manufactory of Mr. Carl H. Schultz, 430-440 First Avenue, New York.

The party was met on the dock by Dr. Schultz and Dr. Hallock, who escorted them to the factory. After doing justice to a luncheon, served by Delmonico, the members were shown through the works by Dr. Schultz, Dr. Hallock, chemist, and Mr. Louis Waefelaer, mechanical engineer.

Established in 1862, these works have now grown to enormous proportions. The factory building is a substantial brick structure, four and five stories in height, covering half a city block. The factory is divided into nineteen departments:

Boiler rooms, engine rooms, siphon-testing department, gas-generating department, buffing department, siphon-filling department, bottle-filling department, pumping station, refrigerating department, water-purifying department, distilling department, cooling department, storage department, chemical department, foundry department, machine shop, electroplating department, carpenter shop, stables.

The carbon dioxide used in the water is generated in heavy lead-lined copper cylinders, from ground dolomite and sulphuric acid, after which it passes through a set of coolers, washers and purifiers to completely remove all impurities. It is stored in a gas-holder, from which it is

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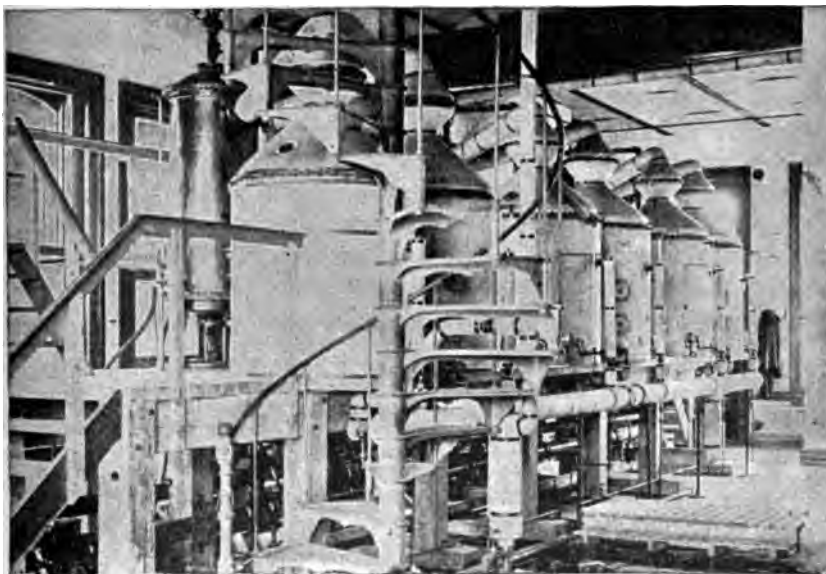
drawn for use in the siphon-filling machines, or compressed in large iron tanks to be used in charging the water in bottles or fountains.

In the building situated on First avenue, are placed the siphon-filling rooms. The solutions containing the numerous ingredients necessary for the production of a correct mineral water are first prepared from standard solutions in the laboratory, and sent over to the siphon-filling department and introduced into large marked vessels. These vessels are filled up to the mark with cold distilled water and thoroughly mixed with a stream of carbon dioxide. Two samples are taken, one from the top and the other from the bottom of the tank, and sent to the laboratory for examination. No siphons can be filled from a solution until it has been examined by the chemist and found to be correct.

The solution flows into a pail, and from this pail it is pumped into the machine. The pump takes the solution in on one side, and the gas in on the other; after compressing the gas into the water, the charged water is forced into a cylinder or reservoir on the top of the machine, from which it is conducted to the siphon.

After many costly experiments Dr. Schultz found that the only way to obtain a pure and tasteless distilled water, was to thoroughly remove all impurities before distilling. In order to remove all suspended matter, the water is pumped through an ingenious filter invented and patented by his deceased son Carl H. Schultz, Jr. It consists of a large vessel suspended on trunnions which can be easily inverted, quickly washed out and afterwards sterilized with live steam, which not only thoroughly cleanses the filtering media, but destroys all organic growth, which has been the great objection to the use of filters. These filters are cleaned and sterilized every day. In the basement are also the boilers, refrigerating machine, cooling coils and hoisting machinery.

The croton water used is pumped in from the street mains and through



DISTILLING APPARATUS.

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the sterilizing filter. Then it passes up-stairs through a set of heat exchangers, which are upright tin-lined copper cylinders containing a large number of one-inch pipes. Here it meets the hot distilled water coming down, thereby cooling the distilled water and heating up the filtered water. On the top floor the water is heated up as much as possible with exhaust steam from the ice machine, then boiled with live steam to drive off the volatile organic matter, the steam being drawn off with an exhaust fan and thrown away. After the removal of the volatile organic matter, the water flows down into the feed-boxes which are constructed to maintain a constant level of water in the stills. The stills, six in number, are arranged in three sets of two each. They are constructed of heavy copper, thoroughly tinned inside. They are about three feet in diameter and four feet in height, surmounted with a dome and separator to prevent any solid particles from being carried over with the steam. They are provided with water and steam gauges, two hand-



ANALYTICAL LABORATORY.

holes on each side for cleaning, and two glass peep-holes on opposite sides on the top. In front of one of the holes a gas-jet is kept burning, which furnishes light to the inside of the still.

The condensation of the steam for distilled water, takes place in tall vertical cylinders, containing a large number of small pipes, through which the cooling water is pumped. Only one condenser is required for two stills. The large amount of cooling effect is obtained indirectly from river water, and to guard against contamination which would result from the river water getting into the distilled water, only croton water

is run through the condensers, and this hot water cooled down for use again by pumping it through a series of coils, over which a stream of river water is kept constantly running.

The distillation is accomplished by steam supplied from two large steam boilers. This steam, which is still very hot when it leaves the still, is conducted to the top floor and used for preheating the water before distillation, thereby utilizing all the heat.

The hot distilled water after leaving the condensers passes down through a set of heat exchangers where it is cooled down as much as possible by the filtered croton water, and then through a second set where it is cooled down to about 40° F. by cold water from the refrigerating machine. It is then stored cold in large covered tanks provided with cotton-plugged vents to prevent any contamination from the air. All the apparatus is constructed of heavily tinned copper, the conducting pipes are made of block-tin and all the valves are silver-plated to guard against any possible metallic contamination.

On the second floor are the laboratories. They consist of two large rooms where the solutions are prepared, and two smaller rooms for analytical work. One of these rooms is especially fitted up for water analysis, and bacteriological work; besides these, there is a small dark room for spectrum analysis and photographic investigation.

The walls are hard finished and painted, and all around is a white pine wainscoting of narrow boards about eight feet high, leaving a space of about three inches from the wall; in this space the water and gas pipes are placed so as not to be seen. The wainscoting is built in sections so any section can be removed, in case it is necessary to get at the pipes for repairs. In the upper part of the partitions are large ground-glass fan-lights which can be opened when extra ventilation is required. The doors have large panels of chipped glass with the names of the different departments cut in. The hood and around the sinks are lined with white tile, giving it a neat appearance, and can easily be kept clean. The front is entirely taken up with large windows furnishing plenty of north light and ample ventilation even in the warmest weather.

The laboratory is well-equipped with all the necessary apparatus, for Dr. Hallock is one of the few fortunate chemists whose employer is generous enough to give him *carte-blanche*.

The luncheon served by Delmonico was unique and deserves special mention. The only appropriate adjective that can adequately describe it is, superb. A pleasant feature was the figures of chemical apparatus with appropriate mottoes designed by Dr. Hallock. One of these represented two retorts with crossed necks and the inscription: "Treat with an excess of C_2H_5OH ," another a picture of a liter flask inscribed, "Fill up to the holding mark."

In returning thanks Dr. Wiley remarked that his idea of the term "mineral waters" had been much enlarged. At the morning session he had suggested that he was not accustomed to lunch on mineral water. That remark he now wished to withdraw entirely. Mr. Schultz responded.

Returning to the steamer the party proceeded to Willet's

Point, where they were welcomed by Colonel King and staff. The visitors were shown an immense electro-magnet, made by using one of the old Rodman guns as a core, and three torpedoes were exploded and photographed. The party then inspected the Museum of Engineering Models and reviewed the parade.

The officers, twenty-five in number, are West Point graduates. There are 425 enlisted men also stationed here. The officers follow the course laid down in the school schedule, while the men are drilled and instructed in the various duties of engineer troops.

THURSDAY, AUGUST 16.

Papers read and discussed :

- Note on the Hardening of Mortar.....WILLIAM P. MASON.
 Note on the Test for Strychnine.....WILLIAM P. MASON.
 The Quality of Water Supplies.....WILLIAM P. MASON.
 The Bacteriology of the Soil as Affected by Depth, Character
 and UseLUCIUS PITKIN.
 Report on Abbreviations of the Names of Metric Terms Used
 by ChemistsWM. H. SEAMAN.
 Some Points in Making Molybdate of Ammonia Solutions for
 Phosphorus Determinations.....CHARLES B. DUDLEY.
 Ucuhuba Fat.....JOSEPH F. GEISLER.
 [This paper was read by title in the absence of the author.]
 A New and Rapid Method of Estimating the Total Proteids
 in MilkE. H. BARTLEY.

At this point the session was adjourned in order that the members might be free to attend the meeting of Section C., of the American Association for the Advancement of Science, to listen to the address by Vice-President T. H. Norton.

At the adjourned session the following papers were read :

- Inspection of Cotton for Use in Gun-Cotton Manufacture.
 CHAS. E. MUNROE.
 Ferric Acid and the Ferrates.....C. A. O. ROSELL.

After a vote of thanks to Dr. F. R. Squibb and Sons, Edward Smith and Co., Carl H. Schultz, Dr. A. P. Hallock, Col. W. H. King, Willet's Point, Mr. Wolf, Disinfecting Plant, Riker's Island, The Long Island Brewery, The Hygienic Ice Co., The Standard Oil Co., The Bergen Point Chemical Works, The Fogarty Gas Co., The Balbach Smelting and Refining Co.,

Feigenspan's Brewery, and the Trustees and Faculty of the Brooklyn Polytechnic Institute, the meeting adjourned.

THURSDAY AFTERNOON.

Some forty or fifty of the chemists visited the Vacuum brewing and the ice-making plants. At the brewing works they were shown through vault after vault full of immense casks of the "Lager," were given a lunch and shown the apparatus for cooling the beer and for forcing carbonic acid gas through it after the fermentation, since by the vacuum method not enough of the gas was formed in it.

At the ice works they were shown the whole process in so far as it could be easily seen: the pumps, the cans in which the water was frozen, with the various stages of the operation which requires about three and a half days for completion, the method of taking the ice cakes out of the cans, etc.

At various times during the meetings, parties of chemists visited the works of Dr. E. R. Squibb and Sons and Edward Smith and Co.

The factory of E. R. Squibb and Sons, for the manufacture of acetic acid and acetates, is a large plant at the foot of Gold street, on the East river water front of Brooklyn. The plant is divided into wood yard on the water front and factory proper in the rear. First were shown the machinery and appliances for cutting up the wood into small billets. Then the loading of this cut wood into iron retorts or cars which run on elevated tracks by means of winches. By these tracks the cars are run into and out of air-bath cells for the distillation of the wood. Each car or retort holds about 2.8 cords of wood, and each oven has twelve cells for as many cars, and the firing and draft flues pass under the floors of the cells, so that the combustion of fuel and its products do not get contact with the retorts or cars of wood. Each retort or car has an eduction pipe which passes through the rear wall of the cell and is connected with a large Liebig condenser. The distillation is conducted at temperatures below 204° C. (400° F.) of the air-bath and the process requires about seven days for each retort. The first day yields water only. Then comes very weak crude acetic acid, and the strength slowly and steadily increases up to about twenty-five per cent. This crude, smoky acid contains but little tar, and when saturated with soda-ash the salt is dried and heated until nearly anhydrous. It is then decomposed with two equivalents of sulphuric acid in a still of peculiar construction with a mechanical stirrer, and yields very strong acetic acid of good quality. This acid is then rectified from bronze stills through glass or silver condensers, yielding the various strengths of fine acid. The commercial grades of acid of different strengths for use in the arts, are made in large stills of ordinary construction from commercial calcium acetate of the markets: decomposed with sulfuric or hydrochloric acid.

The wood after distillation is allowed to cool in the retorts and is then dumped and put up in bags of fifty pounds each, and sold to railroads, steamboats, fire departments, etc., as a kindling material for coal, being

itself an almost perfect fuel, easily lighted, and efficient in very small quantity.

This factory is under the management of Mr. Charles F. Squibb, who was always ready to show it to any of the members of the Society sufficiently interested to accept the invitation of the firm.

The pharmaceutical laboratory was shown to those who visited it during the meeting, chiefly by Dr. E. H. Squibb, who now relieves his father in the management of that part of the business of the firm. It is a large building of five stories, built around a central court yard, and the general plan is to manufacture in the upper stories, store and fill in the next lower, and finish and stock in the next lower, while the ground floor is used for offices, shipping, storage of material, etc. The basement contains the boilers, engines, mills, pumps, drying hoods, etc. The ether apparatus occupies a detached section of the building three stories high, and is fire-proof like many of the other parts. The building is supplied throughout with good apparatus and fixtures too complicated and varied to be comprehended in a short visit, and both apparatus and workmen were clean and orderly. Everything was freely shown and all questions were freely and frankly answered in accordance with the long-established policy of E. R. Squibb and the present policy of E. R. Squibb and Sons.

At the factory of Edward Smith and Co. were seen: First, supplies of raw material; all the commonly known kinds of copal resins, both fossil and recent; also dammar and shellac; linseed oil both raw and prepared for use; refined turpentine having a constant boiling-point, and the still used in redistilling it; the utensils and plant employed in varnish-making, with the operations actually going on; the testing of the finished goods; the most recent improvements in mills, etc., for grinding pigments in varnish and japan; the technical chemical laboratory; and in general, the methods in common use for the management of the manufacturing part of the varnish business. There were to be seen a very large collection of samples of resins and oils, and the kettle in which was made the first batch of varnish ever made in America, besides some old Dutch varnish kettles more than forty years old and still in use.

On Saturday, 18th, the party visited the Standard Oil Works and the Bergen Point Chemical Works at Bayonne, and the Balbach Smelting and Refining Works and Feigenspan's brewery at Newark. This was a joint excursion with Section C. of the American Association for the Advancement of Science. The following account written by one of the party, is abbreviated from one of the Brooklyn daily papers.

The sail down New York Bay was a charming one. The temperature was just right, the atmosphere was clear and the refreshing breeze invigorating.

The first works inspected were the refineries of the Standard Oil Company at Bayonne. The chemists were given every opportunity to inspect the plant, and the processes were carefully explained by the manager, Mr. Van Winkle. The oil comes in through two six-inch pipes, and is started from the pumps under a pressure of about twelve hundred pounds. From the receiving tanks the oil is pumped into a number of stills, each having a capacity of 600 barrels. The products obtained from these stills are a light naphtha, heavy naphtha, white oil, distillate and slops in the order given. The white oil is sold for illuminating purposes.

and the distillate is refined by treatment with acids before it is used for illumination.

It takes three days to run off a "charge" from one of these stills, and it is then thoroughly cleaned before being charged again.

The tarry residue from these stills is treated for lubricating oil and paraffin being pressed through canvas at a temperature of 60° to 65° F., and that which runs out being again subjected to pressure at a much lower temperature.

The distillate from the stills is treated with sulphuric acid, then with steam in an agitator, then with soda and washed to fit it for the market.

After the sludge acid is removed from the tarry product a porous, nearly pure carbon is left which is sold, much of it being used to make the carbon pencils for electric arc lights.

The next visit was to the Bergen Point Chemical Works near by. Here sulphuric acid is made from iron pyrites, and the sludge acid from the Standard Oil Company's Works is refined.

At the Balbach Works, lead ore carrying silver, gold and other metals, is received by steamer from Mexico, and, after treatment, the refined products are shipped to the European market.

The ore is roasted in a reverberatory furnace to remove first the copper and then the antimony as dross.

After these are removed it is put into the softening furnace where other impurities are driven off, and it is then treated by the Parke process for separating the silver and gold from the lead.

The silver, gold, zinc, and some of the lead rise up to the surface and are skimmed off together to be separated from one another by further processes, that which remains being lead, carrying a little zinc and other impurities. This is refined and the pure lead is then ready for the market.

The skimmings from the Parke process are first heated in a crucible of plumbago to drive off the zinc, which comes off as a vapor. This vapor is condensed to liquid zinc, which is run into moulds and allowed to cool.

Silver, lead and gold are then passed on to the crucible by dumping the latter. After cooling, the mass is transferred to a cupel, where it is again melted and a current of air passing over the molten surface changes the lead to litharge which floats upon the surface and is drawn off, leaving the pure silver and gold.

To separate the silver from the gold the combined metals are treated with hot sulphuric acid, which dissolves the silver but does not attack the gold. The silver sulphate thus formed is transferred to a vat in which are placed thin plates of copper. By this means the silver is deposited in the pure metallic state and the copper goes into solution, and is sold to be used in making crystals of copper sulphate.

Many other processes of interest were shown, such as methods of sampling and assaying, charging the blast-furnace, treating the various slags and dross.

The last visit of the day was that to the Feigenspan brewery in Newark, which proved a most interesting part of the day's excursion.

The Board of Directors have granted a charter for a Local Section in New Orleans and vicinity.

MEMBERS PRESENT.

| | | |
|-------------------------|-----------------------|-----------------------|
| H. W. Wiley. | Francis J. Oakes, Jr. | Mary Engle Pennington |
| C. F. McKenna. | G. G. Pond. | Frederick B. Power. |
| F. E. Dodge. | A. P. Hallock. | Charles H. Herty. |
| Wm. Frear. | E. H. Squibb. | H. Pennington. |
| S. A. Lattimore. | H. Endemann. | John C. Hebden. |
| Alfred Springer. | Frederic Read. | S. A. Goldschmidt. |
| Charles E. Munroe. | Herbert S. Bird. | E. R. Squibb. |
| A. A. Breneman. | H. N. Stiles. | E. D. Williams. |
| E. H. S. Bailey. | Charles T. Pomeroy. | C. Chauncey Parsons. |
| Ernest Ellsworth Smith. | S. P. Mulliken. | F. S. Hyde. |
| L. M. Dennis. | Mrs. Lyman F. Kebler. | Franklin Menges. |
| Ferd. A. Sicker. | G. J. Volckening. | Parker C. McIlhiney. |
| Albert H. Welles. | E. H. Bartley. | C. B. Cochran. |
| Rosa Bouton. | T. H. Norton. | F. Hemburg. |
| R. G. Eccles. | W. H. Chandler. | Otis C. Johnson. |
| Henry Souther. | Albert C. Hale. | W. H. Graham. |
| W. A. Noyes. | Edward Hart. | Frank Julian. |
| Jos. A. Hays. | C. Wellington. | W. M. Stiles. |
| R. W. Cornellison. | M. A. Scovell. | Loomis Burrell. |
| William Coutie. | Wm. McMurtrie. | Marcus Benjamin. |
| Frederick J. Wulling. | Edgar F. Smith. | Francis J. Oakes. |
| Owen Louis Shinn. | Francis C. Phillips. | G. Gehring. |
| John Enequist. | Wm. H. Seaman. | A. G. C. Hahn. |
| Lyman B. Hall. | F. W. Spanutius. | Carl H. Schultz. |
| Chas. Baskerville. | Joseph A. Deghuée | Mrs. E. R. Squibb. |
| Peter T. Austen. | George Archbold. | M. Alsberg. |
| Walter M. Saunders. | W. B. Landon. | Lucius Pitkin. |
| Herman G. Schanche. | Edward J. Fuchs. | C. L. Speyers. |
| F. A. Flückiger. | W. M. Grosvenor, Jr. | Jas. Lewis Howe. |
| G. C. Caldwell. | F. W. Mar. | J. W. Provine. |
| Edward B. Voorhees. | R. B. F. Randolph. | Lyman F. Kebler. |
| Herbert B. Baldwin. | C. E. Munsell. | Elwyn Waller. |
| Frank H. Andrews. | Augustus H. Gill. | W. S. Johnson. |
| Frederick G. Zinsser. | Chas. W. Moulton. | Woodville Latham. |
| Leo Backeland. | Mary Coutie Clark. | Peter O. Terheun. |
| W. S. Myers. | Sidney S. Emery. | Morris Loeb. |
| Dalton Parmly. | E. A. de Schweinitz. | Henry A. Mott. |
| T. Lyndon Briggs. | J. H. Wainwright. | Chas. B. Dudley. |
| W. Ernest Wadman. | John. A. Myers. | J. S. Stillwell. |
| A. H. Sabin. | Robert Hall. | W. Gould Levison. |
| W. P. Mason. | Frank Schoney. | Wm. R. Christmas. |
| Walter D. Field. | | |

Proceedings.

By vote of the Council the Winter meeting will be held in Boston, Dec. 27 and 28, 1894.

Authors of papers intended for this meeting should forward their manuscript to the Secretary, Prof. Albert C. Hale, 551 Putnam Ave., Brooklyn, N. Y., as soon as possible.

Notice is hereby given that no paper can be read, except by unanimous consent, unless it has first been submitted to the committee on Papers and Publications. In order that this committee may pass upon communications intelligently they should be sent to Prof. Hale at as early a date as possible.

The Council has accepted the resignation of Dr. H. Carrington Bolton as a member of the Board of Directors.

NEW MEMBERS ELECTED OCTOBER 9.

Burn, E. C., 1722 Vallejo St., San Francisco, Cal.
Burrell, Loomis, Little Falls, N. Y.
Eccles, Dr. Robert G., 191 Dean St., Brooklyn, N. Y.
Fisher, Davenport, 718 Cass St., Milwaukee, Wis.
Herrick, Wm. Hale, 54 Vessey St., New York, N. Y.
Hershey, Aldus N., Waynesboro, Franklin Co., Pa.
Latham, Woodville, 18th St. and 3d Ave., New York, N. Y.
Parsons, C. Chauncey, 43 Sedgwick St., Brooklyn, N. Y.
Power, Frederick B., Fritzsche Bros., 34 Barclay St., New York, N. Y.
Volckening, Gustave J., 675 Lafayette Ave., Brooklyn, N. Y.
Wiltberger, F. K. I., Alexandria, Va.

CHANGES OF ADDRESS.

Buchanan, Dr. C. M., 918 Virginia Ave., S. W., Washington, D. C.
Breyer, Dr. Theodor, 511 Linn St., Peoria, Ill.

De Chalmot, G., Johns Hopkins Univ., Baltimore, Md.
Escher, Paul, care of Solvay Process Co., Syracuse, N. Y..
Falkenau, Louis, 434 California St., San Francisco, Cal.
Graham, Wm. H., 350 Central Ave., East Orange, N. J.
Grosvenor, W. M., Jr., Box 166, Johns Hopkins Univ., Baltimore, Md.
Julian, Frank, care of Ill. Steel Co., South Chicago, Ill.
Lammers, T. L., Townsend, Montana.
Lee, C. T., 146 Franklin St., Boston, Mass.
McCurdy, Chas. W., Univ. of Idaho, Moscow, Idaho.
Meeds, A. D., 427 12th Ave., S. E., Minneapolis, Minn.
Munsell, Dr. C. E., 113 Henry St., Brooklyn, N. Y.
Roth, D. M., Ingleside Place, Walnut Hills, Cincinnati, Ohio.
Saarbach, Ludwig, Ph. D., 12 Old Slip, New York, N. Y.
Schanche, Herman G., P. O. Box 149, Darby, Pa.
Smith, Alex., Univ. of Chicago, Chicago, Ill.
Smith, E. E., 157 E. 14th St., New York, N. Y.
Smith, Edward L., 718 Main St., Worcester, Mass.
Smith, Francis P., Chemist U. S. Navy Yard, New York, N. Y.
Sohon, M. D., Johns Hopkins Univ., Baltimore, Md.
Stokes, H. N., U. S. Geological Survey, Washington, D. C.
Voorhees, Louis A., Box 290, New Brunswick, N. J.
Wyckoff, Geo. H., care of Curtice Bros. Co., Rochester, N. Y.

Proceedings.

OCTOBER 31, 1894.

The General Secretary has been authorized to collect the dues as heretofore; and retain ten per cent. as his compensation.

C. E. Munroe has been elected a member of the Board of Directors in place of H. Carrington Bolton, resigned.

NEW MEMBERS ELECTED OCTOBER 30.

Bogert, Marston T., Flushing, Queens Co., N. Y.
Cleveland, W. P., care of Empire Zinc Co., Joplin, Mo.
Haines, Joseph E., Mickleton, N. J.
Hand, Daniel, 41 Fulton St., Newark, N. J.
Kenan, W. R., Jr., Wilmington, N. C.
McDermott, Thomas E., S. B., care Kavanagh & McDermott, Washington Ave., above 20th St., Philadelphia, Pa.
Riggs, Louis W., Ph.D., Loomis Laboratory, East 26th St., New York, N. Y.
Weston, Robert Spurr, Cinclare Central Factory, Brusly Landing, La.

ELECTED NOVEMBER 10.

Bell, J. Malseed, M.D., 104 North 7th St., St. Joseph, Mo.
Böhm, L. K., 115 Nassau St., New York, N. Y.
Campbell, George F., 47 North Sheffield Hall, Yale University, New Haven, Conn.
Dabney, Chas. W., Jr., Department of Agriculture, Washington, D. C.
Fyster, Geo. S., Ph.D., 19 Central St., Boston, Mass.
Feid, George F., care Wm. S. Merrell Chem. Co., Cincinnati, Ohio.
Hamburger, Avon, North Wales, Montgomery Co., Pa.
Hoffer, John, Jr., 24 North 2nd St., Harrisburg, Pa.
James, Charles, Tacony, Philadelphia, Pa.
Kedzie, Frank S., M.S., Agricultural College, Mich.
McPherson, Wm., Ohio State University, Columbus, Ohio.
Moody, Herbert R., Mass. Inst. Tech., Boston, Mass.
Pitman, Major John, Frankford Arsenal, Philadelphia, Pa.
Sanborn, J. E., Pottstown, Pa.
Schimpf, Henry W., Ph.G., Brooklyn College of Pharmacy, Brooklyn, N. Y.
Stephens, Henry M., Dickinson College, Carlisle, Pa.
Swan, John N., Ph.D., Monmouth College, Monmouth, Ill.
Talbot, Henry P., Mass. Inst. Tech., Boston, Mass.
Van Ingen, D. A., 135 Henry St., Brooklyn, N. Y.
Wedderburn, Augustus, 1420 Penna. Ave., Washington, D. C.

ELECTED NOVEMBER 20.

Bryan, A. Hugh, 748 North Illinois St., Indianapolis, Ind.
Forbes, Fred. B., Experiment Station, Lawrence, Mass.
Hamilton, W. J., care Pueblo Smelting and Refining Co., Pueblo, Col.
Hartman, Prof. Robert, Ph.D., Missionary Institute, Selings Grove, Pa.
Jones, Walter, Ph.D., Purdue University, Lafayette, Ind.
Patterson, Chas. W., 2421 Dearborn St., Chicago, Ill.
Wallace, W. G., B.S., The Globe Soap Works, Cincinnati, Ohio.
Whitfield, J. Edward, 406 Locust St., Philadelphia, Pa.
Wightman, Hugo, 2421 Dearborn St., Chicago, Ill.
Yardley, Samuel S., Stevens Institute, Hoboken, N. J.
Unger, T. S., care Carnegie Steel Co., Munhall, Allegheny Co., Pa.

ASSOCIATES ELECTED OCTOBER 30.

Atkinson, Elizabeth A., Three Tuns, Pa.
McCready, Ernest B., Easton, Pa.
Wetmore, L. L., Englewood, N. J.

ELECTED NOVEMBER 10.

Billard, Jos. D., Jr., 71 Wall St., New York, N. Y.
Sturm, A. B., 2421 Dearborn St., Chicago, Ill.
Weber, C. H., 2421 Dearborn St., Chicago, Ill.

ELECTED NOVEMBER 20.

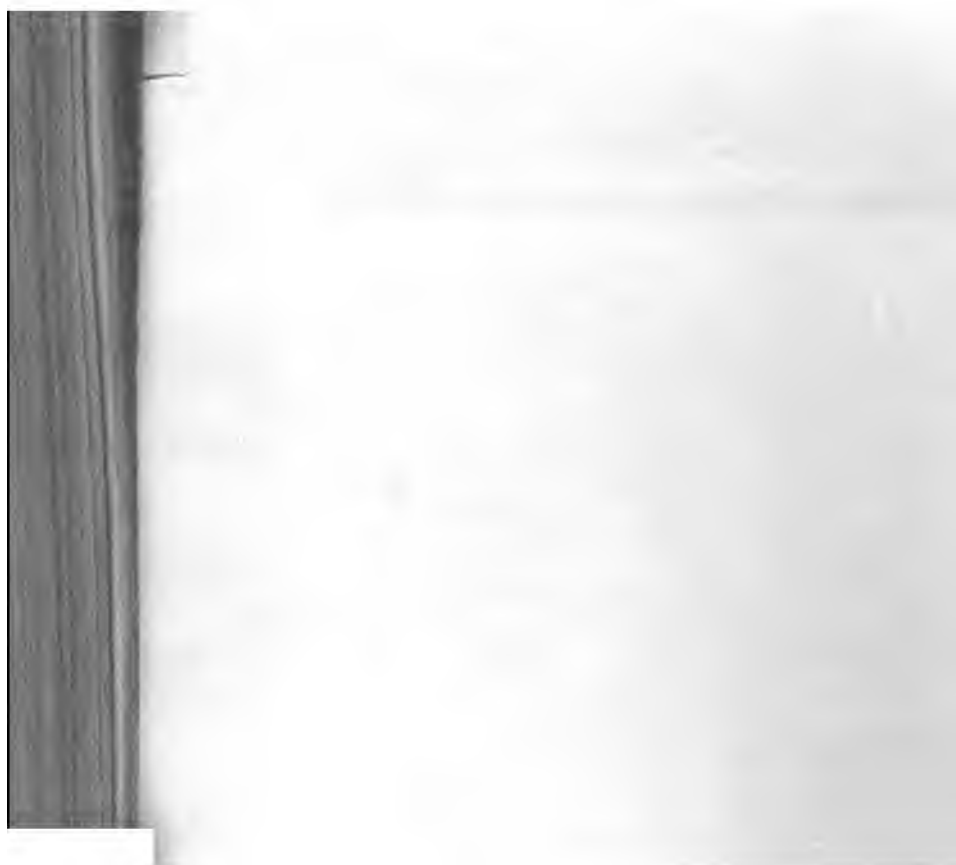
DuPont, Alexis I., Wilmington, Del.

CHANGES OF ADDRESS.

Barton, G. E., Hatfield, Mass.
Cary, J. S., 1760 Monadnock Block, Chicago, Ill.
Coombs, Frank E., Central Teresa, Ceiba Hueca, Manzanillo, Cuba.
Ewell, E. E., 1404 Stoughton St., Washington, D. C.
Latham, Woodville, 32 East 21st St., New York, N. Y.
Lehmann, A., 57 Bayersche St., Port 1, Leipzig, Germany.
Mar, F. W., 32 McDonough St., Brooklyn, N. Y.
Sargent, Geo. W., Boy's High School, Reading, Pa.
Smith, E. E., 157 East 74th St., New York, N. Y.
Spencer, Dr. G. L., 134 Rich Avenue, Mt. Vernon, N. Y.
Willett, Prof. J. E., Augusta, Ga.
Williams, W. J., 1412 Van Buren St., Wilmington, Del.

ADDRESSES WANTED.

Hahn, A. G. C., old address, 4 and 6 New Chambers St., New York, N. Y.
Ray, Victor, old address, Anaconda Electrolytic Refinery, Anaconda, Montana.





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